A Theoretical Study on the Mechanism of the Vibronic Coupling(Dissertation_全文)

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Preface

At the breakthrough from classical alchemy to the modern science of chemistry, the philosophy of the atomic element which had been introduced by Boyle and Dalton has played an important role. This can be said to be the first invention of theoretical chemistry. After this first innovation, chemists recognized shell structures of electrons in atoms and molecules. An especially notable achievement is the periodic classification of atoms by Mendeleev, and the octet rule for the valence electrons in molecules. It is surprising that chemists could derive the valence electronic structure of the chemical bond, from the entirely empirical collections of their experimental results. These are the successful results of the philosophy of the atomic element.

The second innovation was introduced by quantum physicist who established the mechanics which governs the microscopic motion of particles at an atomic level. Above all, the discussion of the valence electronic structure of H_2 molecule by Heitler and London is the pioneering work of the quantum mechanical analysis of electronic structure of chemical bonding. After that, Mulliken and his followers introduced the molecular orbital description of the electronic structures of molecules, and the Hartree-Fock approximation for the electronic structure of molecules was established on

the basis of the molecular orbital method by Roothaan and Hall. The fundamental resolution of the problem of electronic correlation in molecular systems, which has been one of the active fields of theoretical and computational chemistry, was first presented mathematically and physically by Löwdin and Sinanoglu. On the other hand, molecular orbital theories of reactivities of molecules were put forwards first by Fukui and Hoffmann on the basis of the Hückel molecular orbital theory. Their theories predicted stereochemical behaviour of chemical reacting systems successfully and brought the first success of theoretical chemistry over experimental chemistry. The theories of chemical reaction were also developed by introducing the reaction ergodography and the reaction path Hamiltonian model, which uses the steepest descent path of the potential energy surface as one of the global coordinates of the chemical reacting system.

Though these are successful results of the application of quantum mechanics to molecular systems, they also involve a theoretical and philosophical difficulty, whose solution might shed a new light on the field of theoretical chemistry in the future. The most rigorous analysis of a chemical reacting system is the full quantum mechanical treatment of all the particles of which it is composed with their different statistics, i.e. fermions and bosons. This problem is the same as the difficult N-θ problem in quantum field theory. Only

asymptotic solutions are known presently. In the field of molecular physics, the overwhelming magnitude of the masses of the nuclei compared with that of the electrons permits one to use the Born-Oppenheimer approximation for the motion of nuclei where the potential energy surfaces of the different electronic states separate quite well. But, in the region where the potential energy surfaces come near to each other, the simple Born-Oppenheimer approximation breaks down and the difficult N-θ problem appears then. Theoretical chemists have been avoiding the difficulty by the one-sided incorporation of the nonadiabatic effect into the nuclear dynamics. But the finite expansion of the exact total wavefunction by using the Born-Oppenheimer electronic wavefunction may cause significant error. Apart from this problem of accuracy, it is not sufficient for the electronic wavefunction not to be modified by nonadiabatic effects from the point of view of the theoretical picture which the approximation involves. Thus, it would be desirable to renormalize the nonadiabatic effect into the electronic wavefunction, though the full solution of the N-θ problem would be even more desirable.

Even if the nonadiabatic effect and the quantum effect of the molecular vibrations is ignored, the continuous change of the parametric nuclear coordinates may give rise to a characteristic change of the phase factor of an electronic wavefunction, which can be observed by interference if the

cycled system is recombined with another that was separated from it at an earlier time and whose Hamiltonian is kept constant." This problem, which is usually out of the field of theoretical chemists, has been discussed actively by Berry and Simons who have shown that the adiabatic change of the parameter brings in circuit-dependent phase factors. For the many electron system, the problem is not so simple as for the one body problem, because the one electron orbital approximation used there does not ensure that even the one body wavefunction, apart from the phase factor, is adiabatic continuous. The electron orbitals should be made adiabatic continuous, at least, to preserve the orbital concept in this problem. The two problems discussed above can be summarized as (i) the renormalization problem and (ii) the adiabatic continuity problem. These problems are significant in the theoretical study of the coupling of the nuclear dynamics and the electronic motion.

I have studied the mechanism of the vibronic coupling in the chemical reacting system theoretically from this point of view on the basis of the traditional quantum chemical methods. Reaction ergodography is also useful sometimes for this study. In part I of this thesis, the Hartree-Fock equation is modified to be capable of representing the effect of vibrational motion on the electronic orbitals. The electron orbitals obtained from this dynamic Fock equation include the

effect of the kinetic energy of nucleus and the quantum effect of the molecular vibration as well. The energy exchange between molecular vibrations and electronic motions can be considered to be small enough to be neglected in the stable molecule. By regarding the nonadiabatic term in the dynamic Fock equation as a perturbation term, the zero-th order solutions become adiabatic electron orbitals. Then I focussed my attention on the quantum effect. The electron densities which reflect the quantum effect of the molecular vibration are analyzed, analytically and numerically, for diatomic molecules and an aromatic molecule. The significant features of the charge redistribution accompanying an excitation of a molecular vibration are demonstrated both qualitatively and quantitatively. The mechanism of the vibronic coupling in the intense infrared radiation field is also discussed. In part II of this thesis, the dynamic charge redistribution accompanying the motions of a wavepacket along the Intrinsic Reaction Coordinate is studied. The vibrationally induced dipole fluctuation between the two fragments of the chemical reacting species is also studied. The effect of the isotopic substitution and the vibrational mode specific feature of a chemical reaction are analyzed by using the dynamic electron transfer and the vibrationally induced dipole fluctuation mentioned above. This will be of help to understand the dynamic electronic aspect of the chemical reaction dynamics,

such as infrared laser induced chemical reactions. The existence of the novel intermolecular force originated in the vibronic coupling is also discussed. In part III of this thesis, the rearrangement of electrons accompanying the chemical reaction is studied by using the electron orbitals which are transformed so as to make them adiabatic continuous accompanying the parametric change of nuclear coordinates. Some quantities related with the spatial part of one body wavefunctions apart from their phase factors are analyzed. First, the spatial expansions of electron orbitals are traced along the reaction coordinate. Second, the change of the orbital energies and the occupation numbers of the transformed electron orbitals are traced to picture the characteristic rearrangement of electrons accompanying chemical reactions in terms of the orbital energy-occupation number correlation diagram. The time-dependent perturbation method is also applied to introduce the nonadiabatic effect into the occupation number of the electron orbital. Finally, a general summary of the present thesis is given at the end.

Acknowledgements

The present thesis is the summary of my studies from 1982 to 1986 at the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University.

I wish to express my sincere gratitude to Professor Tokio Yamabe and Dr. Akitomo Tachibana for their kind guidance, stimulating discussions full of philosophical suggestions, and continuing encouragements throughout this work. I also cordially thank Professor Kenichi Fukui for his encouragement. Thanks are also made to Dr. Kenzi Hori for his useful suggestions, generous permission to use his program, cooperation and discipline in coding the requisite new subroutines which are linked with the Gaussian 80 program, and warmhearted encouragement. Dr. Hiroyuki Teramae is also acknowledged for his useful suggestions, sincere elucidation about the programming techniques, and generous permission to use his ab initio molecular orbital program. Thanks are also due to Professor Hiroshi Taniguchi, Mr. Masaru Kohno, and Mr. Shogo Ikeuchi for their joint effort and to the members of Quantum Chemistry Group; Dr. Masahiko Koizumi, Mr. Masataka Nagaoka, Mr. Takayuki Inoue, and Mr. Hiroyuki Fueno and many other members, for their active discussions.

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Center of Institute for Molecular Science, of which staffs I would like to thank. I would like to express my deep appreciation to Prof. Teijiro Yonezawa and Prof. George G. Hall for their comments in the examination to fulfill the requirements for the Degree of Engineering. To Professor Hall, I also wish to express my sincere gratitude for his valuable suggestions. Finally, it is also my pleasure to thank my parents Teruichi Asai and Emiko Asai for their understanding and encouragements.

PART I

The Dynamic Coupling of the Electron Density and the Molecular Vibration

Chapter 1

Introduction

Traditional study of the electronic structure of molecules lays, as the foundation, the Born-Oppenheimer adiabatic approximation which treats the motions of electrons and nuclei at quite different stages in the theoretical framework. This approximation relies on the fact that the mass of a proton is ca. 1833 times that of an electron and the deviations are proportional to the fourth root of the ratio of the masses. Indeed, the approximation works quite well when the separation of the potential surfaces of the different electronic states are large, and narrow separation will sometimes give the breakdown of the approximation.

There is a straightforward conclusion from the diagonal correction to the Born-Oppenheimer adiabatic approximation which reflects the nonadiabatic correction only into the dynamics of the nuclei. The electronic wavefunctions with the Born-Oppenheimer clamped-nuclei approximation are used as the basis set wavefunctions for the total Schrödinger equation of molecule and the resultant Schrödinger equations of nuclear motion for each electronic state with the diagonal nonadiabatic correction terms and interstate coupling terms are obtained by this way. The full solution of the equations needs some tricky tactics which are not valid strictly in the

general polyatomic case. Moreover, this method needs a truncation of the expansion, and an artificial classification of the vibronic bands. All of these have the possibility of causing a significant error. Moreover, the actual numerical calculation suffers from cumbersome difficulties.

In addition to this problem, it is desirable to formulate an electronic wavefunction which reflects the dynamics of the nuclei also from the point of view of the theoretical picture which the approximation involves. In this formulation, the quantum effect of the nuclear motion should be included naturally. The modified electronic wavefunction which reflects the nuclear dynamics, i.e. the kinetic energy and the quantum effect will enable one to obtain a detailed picture of the dynamics of electrons and nuclei. It might be interesting then to infer the mechanism of electric conductivity from the first principles when the molecular vibration cannot be neglected.

It should be emphasized that though an exchange of the kinetic energies of electrons and nuclei is expected to be small in stable molecules, the quantum effect of the molecular vibrations should not be neglected. This is because all molecules have at least the zero-point vibrational energies and the quantum effect of the molecular vibration on the electronic motion cannot be treated by perturbational techniques and hence can hardly ever be resolved. The effect would be interesting in the light of the stable quantum

mechanical structure of a nonrigid molecule which has been one of the recent interests.

In chapter 2 of this part (Chem. Phys. Lett., 106,36(1984)), the variational principle used in the Hartree-Fock approximation for the electronic structure of a molecule is extended so as to obtain the dynamic Fock equation which determines the dynamic electron orbitals reflecting the kinetic energy and the quantum effect of the molecular vibration. The dynamic electron densities which reflect the quantum effect of the molecular vibrations are analyzed both analytically and numerically for H_2, and $C_3H_3^+$ molecules. The characteristic change of the electron density accompanying the excitation of the molecular vibration, which is named the dynamic electron transfer is discussed.

In chapter 3 of this part (J. Chem. Phys., 80,6170(1984)), some properties of the dynamic Fock equation obtained in chapter 2 are discussed. Also the thermodynamical and time dependent properties of the dynamic electron transfer are discussed analytically. The dynamic electron transfers of H_2, HD, HT, HF, and HCl are calculated numerically to discuss the mass dependencies and the orbital contributions to them. The time dependent dynamic electron transfers accompanying the coherently oscillating wavepacket are discussed for these molecules, too.

In chapter 4 of this part (to be submitted for

publication), the isomerization reactivities and the stabilities of the vinylcation are investigated for the two geometrical isomers; open chain and triangular forms. These investigations make it possible to infer the possibility of the participation of the triple bond to the cationic center in the photo-solvolytic reactions where the elementary reaction mechanism is still unknown today. The dynamic electron transfers as well as the energetics are analyzed for these investigations.

Finally, the conclusions obtained from chapter 2 to chapter 4 are discussed and summarized in chapter 5 of this part.

Chapter 2

Dynamic Coupling of Electronic Motion and Molecular Vibration

Recently, the dynamic characteristics of molecular vibration have received much attention in studying various aspects of reaction dynamics in polyatomic molecular systems[1]. Particularly, the vibrational relaxiation of molecules or the mode-specific chemical reactivity in laser chemistry are current interests in terms of the intramolecular or intermolecular energy transfer problems.

In the study of the dynamic treatment of the nonrigid molecular properties, the Born-Oppenheimer (BO) adiabatic approximation of electronic motion has been the first one of the guiding principles. The BO approximation treats the electronic and nuclear motions in a fundamentally different way. The need for developing new methods going beyond the traditional BO approximation has been stressed recently by several authors[2-8]. The concept of the dynamic "structure" of non-rigid molecular system has been of special interest. In this connection the non-BO treatment of electron density theory has been studied[9]. The dynamic coupling between electronic states and vibrational motion has been a major subject in the study of radiationless transition process[10].

The main subject of the this chapter is a dynamic analysis of electronic motion in the course of the internal motion of the molecular system. A general non-BO equation for an electron orbital is formulated for the study of the dynamic electronic structure. We demonstrate an interesting "additive" property of a normal vibration of a molecular system on the dynamic electronic structure.

The electron orbitals $\{\psi_j\}$ satisfy the orthonormal conditions

$$\langle \Psi_{nuc} \mid \langle \psi_i \mid \psi_j \rangle \mid \Psi_{nuc} \rangle = \delta_{ij}, \tag{1}$$

where Ψ_{nuc} denotes the nuclear wavefunction. These are determined by the variational principle using the energy functional

$$E = \langle \Psi \mid H \mid \Psi \rangle - \sum_{i,j} \varepsilon_{ij} \langle \Psi_{nuc} \mid \langle \psi_i \mid \psi_j \rangle - \delta_{ij} \mid \Psi_{nuc} \rangle$$

$$- \lambda (\langle \Psi_{nuc} \mid \Psi_{nuc} \rangle - 1), \tag{2}$$

where H is the molecular Hamiltonian, Ψ is the molecular wavefunction and $\{\varepsilon_{ij}\}$ and λ are Lagrange multipliers. The variational wavefunction Ψ thus obtained may be represented in the usual expansion form for the analysis of the dynamic correlation of the electronic and nuclear motions(see, for example, ref.8). Determination of the expansion coefficients is now incorporated into the variational calculation of $\{\varepsilon_{ij}\}$ and λ. Thus, ψ_j may be represented as a linear combination of an appropriate set of electron orbitals $\{\varphi_r\}$ as

$$\psi_i = \sum_r \varphi_r c_{ri} , \tag{3}$$

where c_{ri} denote the expansion coefficients determined by the variational condition $\partial E/\partial c_{ri} = 0$ and its complex conjugate. The resulting dynamic Fock equation is simplified if we adopt the single-determinant electronic wavefunction with an orthonormal basis set, and is then given as

$$\mathbf{f}\mathbf{c}_i = \varepsilon_i \mathbf{c}_i . \tag{4}$$

In this expression, the dynamic fock operator **f** is

$$f = \langle \Psi_{nuc} \mid F + \Delta \mid \Psi_{nuc} \rangle , \tag{5.a}$$

where **F** is the usual Hatree-Fock operator and Δ is the non-adiabatic coupling operator[11]. If the molecular motion is represented as a one-dimensional normal coordinate Q and the nuclear wavefunction is chosen to be real, then the matrix element of operator Δ is

$$\begin{aligned}
\Delta_{rs} &= (1/2)\langle \partial\varphi_r/\partial Q \mid \partial\varphi_s/\partial Q \rangle \\
&+ (1/2)\sum_t \sum_u \sum_j^{occ} c_{tj}^* c_{uj} \\
&\times (\langle \partial\varphi_r/\partial Q \mid \varphi_s \rangle \langle \varphi_t \mid \partial\varphi_u/\partial Q \rangle \\
&+ \langle \partial\varphi_t/\partial Q \mid \varphi_u \rangle \langle \varphi_r \mid \partial\varphi_s/\partial Q \rangle \\
&- \langle \partial\varphi_r/\partial Q \mid \varphi_u \rangle \langle \varphi_t \mid \partial\varphi_s/\partial Q \rangle \\
&- \langle \partial\varphi_t/\partial Q \mid \varphi_s \rangle \langle \varphi_r \mid \partial\varphi_u/\partial Q \rangle) ,
\end{aligned} \tag{5.b}$$

If the exchange of energy between the electronic motion and the nuclear motion is small, then it may be reasonable to choose the usual adiabatic Hartree-Fock orbitals along the

normal mode as the $\{\varphi_r\}$; the operator Δ may then be neglected. This results in the simple solution

$$c_{ri}=\delta_{ri} \ and \ \varepsilon_i=\langle \Psi_{nuc} \mid F_{ii} \mid \Psi_{nuc} \rangle . \tag{6}$$

The dynamic electron orbitals is then given by the one-term expansion and the energy is merely the average value of the adiabatic orbital energy.

Let us analyze the mechanism of electron redistribution induced by the vibrational motion. The dynamic distribution of electron density is

$$\langle \rho \rangle_\nu=\langle \Psi_\nu \mid \rho \mid \Psi_\nu \rangle , \tag{7}$$

where ρ denotes the distribution of electron density which is obtained by solving the dynamic fock equation(4) using the vibrational wavefunction Ψ_ν with quantum number ν. The dynamic electron distribution changes as the vibrational mode is excited. If the vibrational mode is harmonic, then the dynamic electron transfer may be proved to be "additive"[11]:

$$\langle \rho \rangle_{\nu+1} \sim \langle \rho \rangle_\nu + \Delta \langle \rho \rangle , \tag{8a}$$

with

$$\Delta \langle \rho \rangle = \{ 1/(2\omega) \} \ \partial^2 \rho(0)/\partial Q^2 \tag{8b}$$

In this expression, ρ is approximated as the Taylor series expansion up to second order with respect to Q, where ν denotes the vibrational frequency. The "additive" property of the dynamic electron transfer is so fundamental and general that it may be proved by a carefully arranged experiment for example by using mode-specific activation of the molecular

system[11]. It is closely connected with the temperature effect of the dynamic deformation density[12] and the time-dependent property of the dynamic electron transfer[11].

In order to illustrate the present theory, the "additive" structure of H_2 and cyclic $C_3H_3^+$ molecular systems are demonstrated. The ab-initio molecular orbital calculations were performed by using GAUSSIAN 80[13] with the 4-31G basis set[14] together with new subroutines to treat the dynamic electron structure. The vibrational modes are calculated using HONDOG[15]. Since the system is considered to be fairly "rigid", the operator is neglected and the solution of eq.(6) is used.

In Fig.1, the dynamic electron transfer of H_2 is shown as the difference from the value of the dynamic electron density corresponding to the zero-point vibration. As the vibrational number increases, the dynamic electron transfer becomes large and clearly demonstrates the "additive" property predicted by eq.(8).

The dynamic electron transfer of $C_3H_3^+$ is shown in Fig.2. The in-plane doubly degenerate vibrational modes ν_1 and ν_2 are examined. By excitation of ν_1 mode, "additive" dynamic electron accumulation occurs along the x-axis, and by excitation of the ν_2 mode along the y-axis. These modes are coupled to yield an angular momentum which is perpendicular to the molecular plane[17]. If mode-specific excitation of a vibrational mode is designed, then it is expected that dynamic

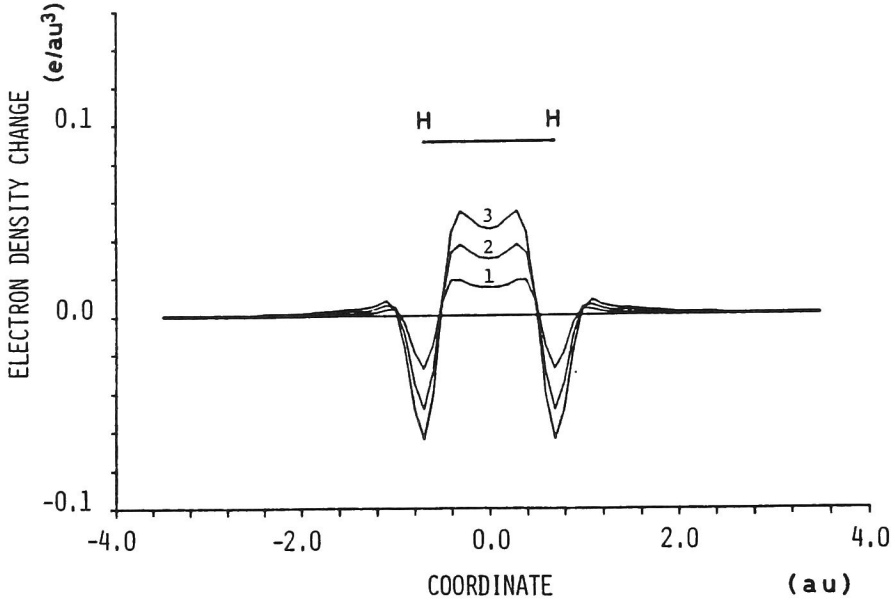

Fig. 1. Dynamic electron transfer $\langle\rho\rangle_\nu - \langle\rho\rangle_0$ of the H_2 molecule along the molecular axis (in e/bohr^3). The nuclei in the equilibrium configuration are located at ±0.6895 bohr. The vibrational frequency is 4650.8 cm^{-1}. Experimental values of the equilibrium distance and vibrational frequency are 1.4016 bohr and 4395.2 cm^{-1}, respectively [16]. The numbers in the figure denote vibrational quantum numbers.

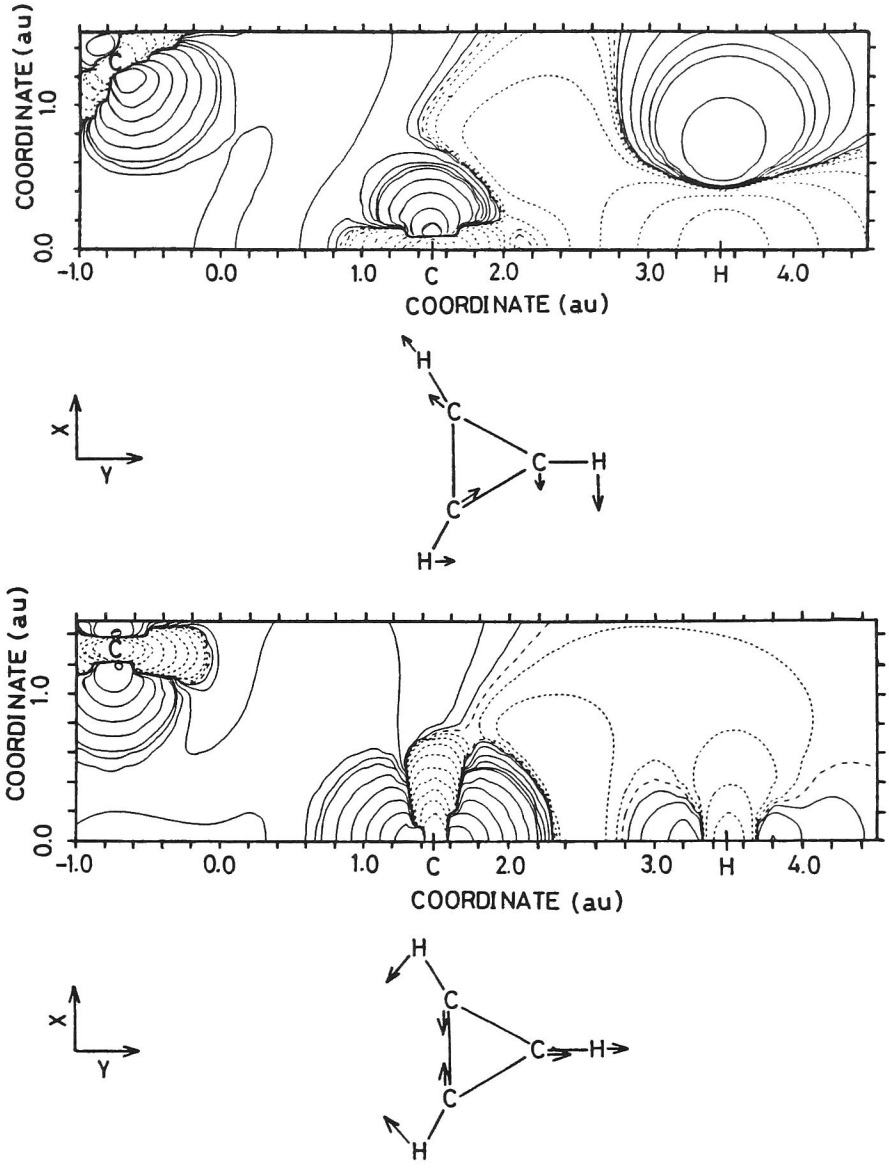

Fig. 2. Dynamic electron transfer $\langle\rho\rangle_3 - \langle\rho\rangle$ of the cyclic $C_3H_3^+$ ion in the molecular plane; (a) for the ν_1 mode and (b) for t ν_2 mode. The nuclei in the equilibrium configuation drawn in the contour map are located (from left to right) at C(1.286, −0.742, 0.0), C(0.0, 1.485, 0.0) and H(0.0, 3.405, 0.0), respectively (in bohr). The vibrational frequency is 1038 cm^{-1}. Sol lines and dotted lines correspond to an increase and a decrease of the dynamic electron transfer, respectively. The broken lin shows null transfer. The values of the contours are −1.0, −0.3, −0.1, −0.03, −0.01, -3.0×10^{-3}, -1.0×10^{-3}, $-3.0 \times 10^{-}$ -1.0×10^{-4}, 0.0, 1.0×10^{-4}, 3.0×10^{-4}, 1.0×10^{-3}, 2.0×10^{-3}, 3.0×10^{-3}, 4.0×10^{-3}, 1.0×10^{-2}, 3.0×10^{-2}, 0.1, and 1.0 e/bohr^3, respectively.

electron transfer having non-zero angular momentum may be induced by suitably coupled molecular vibrations. This may yield an interesting dynamic effect on the σ-electron participation in the ring current model of aromatic compounds[18] or the electron conductivity of conjugated systems.

Three-dimensional dynamic electronic structure including the direction perpendicular to the vibrational mode and the application to the chemical reaction systems are of interest and will be published elsewhere.

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Chapter 3

Dynamic Analysis of Electron Density in the Course of the Internal Motion of Molecular System

I. INTRODUCTION

Recent developments in laser chemistry have revealed the important role of molecular vibration in chemical reaction dynamics or energy transfer and its randomization processes. In this connection, there have been many experimental studies on mode-selective reactions[1-3] and mode-specific enhancement[4] of chemical reactions. Therefore, much attention have been focused on an important role of anharmonicity of molecular vibration[5] in order to understand these phenomena. The important role of anharmonicity of molecular vibration and chaotic feature of molecular dynamics on potential energy hypersurface[6-10] have received much attention , especially in conjunction with nonlinear classical mechanics and ergodic problems in fundamental statistical mechanics. Quantum mechanical treatments have also been applied to this problem, in terms of the stability of state.[11-15] Also from a theoretical point of view, Reaction Path Hamiltonian[16,17] was derived on the basis of the reaction coordinate defined by Fukui, called the intrinsic reaction coordinate(IRC),[18] and

has been utilized to describe the distinct roles of the vibrational modes in polyatomic chemical reaction processes. From this analysis, the vibrational modes normal to the reaction coordinate were classified into two categories.[19] They are the "system modes" which are closely coupled to reaction coordinate and the "bath modes" which do not seriously intervene in the reaction process and are consumed only to raise the effective potential energy of the reacting system. Moreover, the coupling between IRC and its perpendicular modes was analyzed by use of a vibrational frequency correlation diagram[20,21] in order to discuss the possibility of mode specific reaction or to calculate state-selected reaction rates.

In the liquid phase, vibrational motions of solvent molecules which do not intervene in the reaction coordinate should be treated as the "bath modes".[22] The statistical treatment of the effect determines the temperature-dependent effective potential. The time-dependent treatment of the chemical reaction dynamics has also been developed in terms of the generalized Langevin equation.[23] Thus, the great importance of molecular vibrations in chemical reaction dynamics has been largely stressed.

On the other hand, much attention have been focused on the dynamic coupling between electronic states and vibrational motions.[24] It is because the electron-phonon coupling plays an

important role in the radiationless transition processes observed in the condensed phase, the electron and proton transfer in biological systems, or the electric conductivity in organic and inorganic materials. Moreover, electronic structures of the nonrigid molecular systems[25-30] such as Jahn-Teller effect and pseudorotation are largely affected by the nuclear motions. The concept of stable "structure"[31,32,33] of nonrigid molecular system has been one of the recent interests. And there are a series of works by Peyerimhoff and her collaborators which treat the highly vibrationally excited states of organic molecules.[34]

So as to understand these kinds of vibronic phenomena, more advanced treatment beyond the usual Born-Oppenheimer(BO) approximation is highly recommended. The traditional method is, in the most rigorous sense, insufficient because all molecules have at least zero-point vibration and nuclei are not fixed frozen. Therefore, the necessity for developing new methods including the vibrational effect has been stressed recently by several authors.[31,35-38]

In this chapter, therefore, we develop a method to understand the dynamic characters of electronic structure in the course of the internal motion of molecular system. It is a general non-BO equation of electron orbital formulated for the dynamic study of electronic motion.[39] We also analyze a quantity, an averaged electron density with respect to

molecular vibration, and demonstrate an interesting "additive" property of the electron density with respect to vibrational quantum numbers. The time-dependent process of the electron transfer is also analyzed, using coherent-state of normal vibration.[40] The theoretical prediction based on this "additive" property will be important for the determination of the dynamic deformation density of molecules whose theoretical analysis itself has also received much attention.[41,42]

II. VIBRATION-COUPLED ELECTRONIC MOTION

A. Vibration-coupled electronic structure

In terms of the Hohenberg-Kohn theorem,[43] the adiabatic electronic energy is determined as the functional of the electron density although the functional form itself has not been found. Hence, at present, we can not rigorously obtain the electronic energy by variationally optimizing the electron density itself.[44] Instead, we usually obtain the electron orbital and adopt the fundamental picture that the correlation of the orbital motion of electron determines the whole dynamics of electron assembly.[45]

If the nonadiabatic coupling is taken into account, then the orbital motion of electron will be modified. The modification is determined by the dynamic mode of nuclear motion. Then, the electron orbitals $\{\psi_j\}$ satisfy the

orthonormal conditions in the following form:

$$\langle \Psi_{nuc} \mid \langle \psi_i \mid \psi_j \rangle \mid \Psi_{nuc} \rangle = \delta_{ij}, \tag{1}$$

where Ψ_{nuc} denotes the nuclear wave function. This shows that the electron orbital is not merely considered the one-particle function in the adiabatic treatment of the electronic state. The electron orbital is now considered the correlation function with respect to the electronic motion and the nuclear motion. These are determined by variational principle using the energy functional

$$\varepsilon = \langle \Psi \mid H \mid \Psi \rangle - \sum_{i,j} \varepsilon_{ij} \langle \Psi_{nuc} \mid \langle \psi_i \mid \psi_j \rangle - \delta_{ij} \mid \Psi_{nuc} \rangle$$

$$- \lambda (\langle \Psi_{nuc} \mid \Psi_{nuc} \rangle - 1), \tag{2}$$

where H is the molecular Hamiltonian, Ψ is the molecular wave function, and where ε_{ij} and λ are the Lagrange multipliers. Since the energy of the molecular system is real, we should require

$$\varepsilon^* = \varepsilon, \tag{3.a}$$

hence, we have

$$\varepsilon_{ij}{}^* = \varepsilon_{ji}; \quad \lambda^* = \lambda. \tag{3.b}$$

The variational wave function Ψ thus obtained may be represented in the usual expansion form for the analysis of the dynamic correlation of the electronic motion and the nuclear motion:

$$\Psi = \sum_{I,J} C_{IJ} \Psi_{elec,I} \Psi_{nuc,J}, \tag{4}$$

where $\{\Psi_{elec,I}\}$ and $\{\Psi_{nuc,J}\}$ denote the appropriate sets of

electronic wave functions and nuclear wave functions, and where $\{C_{IJ}\}$ denotes the set of expansion coefficients. The expansion coefficients are usually determined by perturbation theory and variational treatment. The determination of the expansion coefficients is now incorporated into the variational calculation of ε_{ij} and λ. Thus, the ψ_j may be represented as the linear combination of appropriate set of electron orbitals as follows:

$$\psi_i=\sum_r \varphi_r c_{ri}\,, \tag{5}$$

where $\{c_{ri}\}$ denote the expansion coefficients determined by the variational condition $\partial\mathcal{E}/\partial c_{ri}=0$ and its complex conjugate. The resulting dynamic Fock equation is simplified if we adopt the single determinantal electronic wave function and real nuclear wavefunction, and is then given as follows:

$$\boldsymbol{f}\boldsymbol{c}_i=\varepsilon_i \boldsymbol{c}_i \tag{6}$$

In this expression, the dynamic Fock operator $\boldsymbol{f}$ is represented as follows:

$$\boldsymbol{f}=\langle \Psi_{nuc} \mid \boldsymbol{F}+\Delta \mid \Psi_{nuc}\rangle \tag{7.a}$$

with

$$\Delta_{rs} = (1/2)\langle \partial\varphi_r/\partial Q \mid \partial\varphi_s/\partial Q\rangle$$

$$+ (1/2)\sum_t\sum_u\sum_j^{occ} c_{tj}^{*}c_{uj}$$

$$\times(\langle \partial\varphi_r/\partial Q \mid \varphi_s\rangle\langle\varphi_t \mid \partial\varphi_u/\partial Q\rangle$$

$$+\langle \partial\varphi_t/\partial Q \mid \varphi_u\rangle\langle\varphi_r \mid \partial\varphi_s/\partial Q\rangle$$

$$-\langle \partial\varphi_r/\partial Q | \varphi_u \rangle \langle \varphi_t | \partial\varphi_s/\partial Q \rangle$$

$$-\langle \partial\varphi_t/\partial Q | \varphi_s \rangle \langle \varphi_r | \partial\varphi_u/\partial Q \rangle), \qquad (7.b)$$

where F, Δ, and Q denote the usual Hartree-Fock operator, the nonadiabatic coupling operator, and the normal coordinate of internal motion, respectively. By solving Eq. (6) self-consistently we obtain the non-BO electron orbital. It takes explicitly account of the nonadiabatic coupling.

If the exchange of energy between the electronic motion and the nuclear motion is small, then it may be reasonable to choose the usual adiabatic Hartree-Fock orbitals along the normal mode as the φ_r, and then the operator Δ may be neglected. This results in the following simple solution:

$$c_{ri}=\delta_{ri} \qquad (8.a)$$

and

$$\varepsilon_i=\langle \Psi_{nuc} | F_{ii} | \Psi_{nuc} \rangle . \qquad (8.b)$$

Then the dynamic electron orbital is represented by the one-term expansion and the energy is nothing but the average value of the adiabatic orbital energy.

B. "Additive" property

Let us analyze the mechanism of electron redistribution induced by the vibrational motion of molecular system. This analysis is meaningful if we know the position probability density $P_{nuc}=\Psi_{nuc}^{*}\Psi_{nuc}$ of the constituent nuclei which take part

in the normal vibration. Using the harmonic approximation of the normal vibration, the dynamic distribution of the electron density is given as follows:

$$\langle \rho \rangle_\nu \equiv \int \rho P_\nu dQ \tag{9.a}$$

with the vibrational quantum number ν

$$P_\nu = \Psi_\nu^* \Psi_\nu , \tag{9.b}$$

where ρ denotes the distribution of the electron density which is the diagonal element of the first order density matrix, $\gamma_{(1)}(1 \mid 1)$, by using the solution of the dynamic Fock equation (6). The electron distribution changes as the vibrational mode is excited. This electron redistribution defines the "dynamic electron transfer". As a first step to study this problem, we shall use the approximate solution of Eq. (8) and disclose the remarkable "additive" property of the "dynamic electron transfer".

If we express ρ in terms of Taylor series expansion with respect to the normal coordinate, then we have

$$\rho(Q) \sim \rho(0) + (\partial \rho / \partial Q)(0) Q + (1/2)(\partial^2 \rho / \partial Q^2)(0) Q^2 , \tag{10}$$

Substituting Eq. (10) into Eq. (9), we obtain approximately

$$\langle \rho \rangle_\nu \sim \rho(0) + (1/2\omega)(\partial^2 \rho / \partial Q^2)(0)(\nu + 1/2) , \tag{11}$$

where ω denotes the vibrational frequency. This reveals the interesting "additive" property of the dynamic electron transfer. Indeed, an amount of electron transfer is approximately constant if we excite the normal mode by constant energy;

$$\langle\rho\rangle_{\nu+1}\sim\langle\rho\rangle_{\nu}+\Delta\langle\rho\rangle\,, \tag{12.a}$$

where

$$\Delta\langle\rho\rangle=(1/2\omega)(\partial^2\rho/\partial Q^2)(0)\,. \tag{13}$$

It should be noted that the zero-point vibration itself brings about half the amount of the dynamic electron transfer $\Delta\langle\rho\rangle$:

$$\langle\rho\rangle_0\sim\rho(0)+(1/2)\,\Delta\langle\rho\rangle\,. \tag{13}$$

The "additive" property of the dynamic electron transfer is so fundamental and general that it is considered to be proved by carefully arranged experiment, for example, by using the mode-specific activation of molecular vibration.

The temperature dependence of the dynamic electron transfer may be estimated simply by using the "additive" property as follows:

$$\overline{\langle\rho\rangle}_T\equiv\sum_{\nu}\langle\rho\rangle_{\nu}\exp(-\beta E_{\nu})/\sum_{\nu}\exp(-\beta E_{\nu})\,,$$

$$\sim\langle\rho\rangle_0+\Delta\langle\rho\rangle\,(1/2)\coth z, \tag{14.b}$$

with

$$z=(1/2)\beta\omega \tag{14.c}$$

$$\beta=1/kT \tag{14.d}$$

where E_{ν}, k and T denote the vibrational energy, the Boltzmann constant, and the temperature of vibration, respectively. And we have the limit as T tends to zero:

$$\overline{\langle\rho\rangle}_T\sim\langle\rho\rangle_0+\Delta\langle\rho\rangle\exp(-\beta\omega)\,;\ T\sim0 \tag{15}$$

which shows the important nonadiabatic contribution of the zero-point vibration at low temperature as is given in Eq.

(13). It should be noted that this simple temperature effect of the dynamic electron transfer will play an important role particularly for the determination of the dynamic deformation density in the field of solid state physics.[41,42]

C. Time-dependent aspect

It is interesting to compare the "additive" property of the dynamic electron transfer with time-dependent treatment of molecular vibration. The time-dependent treatment is based on the time-dependent Schrödinger equation:

$$i(\partial/\partial t)\Psi_{nuc}=H_{nuc}\Psi_{nuc}, \tag{16}$$

where H_{nuc} is the nuclear Hamiltonian of the normal vibration. Adopting the harmonic approximation of the normal vibration, we have the coherent state as the solution of Eq. (16):

$$\Psi_{nuc}=\Psi_{coherent}, \tag{17}$$

where $\Psi_{coherent}$ denotes the wave function of the coherent state, and it can be expressed as follows:

$$\Psi_{coherent}=(\omega/\pi)^{1/4}\exp[-(1/2)\omega(Q-Q_0\cos\omega t)^2 - i\{(1/2)\omega t+\omega QQ_0\sin\omega t-(1/4)\omega Q_0^2\sin 2\omega t\}] \tag{18}$$

The coherent state is represented as the wave packet of Gaussian position probability density which is initially centered at $Q = Q_0$. It should be noted here that the coherent state has recently been used for the study of the time-dependent aspect of reaction dynamics in the electronically and vibrationally excited states.[13,46-48] With

respect to the distribution of position probability density, the vibrationally highly excited state resembles the classical model of the harmonic oscillator.

The averaged value of ρ is then given as

$$\langle \rho \rangle_{coherent} = \int \rho P_{coherent} dQ, \tag{19.a}$$

where

$$P_{coherent} = \Psi_{coherent}^{*} \Psi_{coherent} \tag{19.b}$$

Substituting Eq. (10) into Eq. (19a), we obtain

$$\langle \rho \rangle_{coherent} \sim \rho(0) + (\partial \rho / \partial Q)(0) Q_0 \cos\omega t + (1/2)(\partial^2 \rho / \partial Q^2)(0) \{ (1/2\omega) + (Q_0 \cos\omega t)^2 \} . \tag{19.b}$$

If we take the average over one period τ of the normal vibration, then we have

$$\overline{\langle \rho \rangle}_{wavepacket} \equiv (1/\tau) \int_0^{\tau} \langle \rho \rangle_{wavepacket} dt \tag{21.a}$$

$$\sim \rho(0) + (1/2\omega)(\partial^2 \rho / \partial Q^2)(0)(\nu_c + 1/2) \tag{21.b}$$

where

$$\nu_c = (1/2)\omega Q_0^2 . \tag{21.c}$$

It is interesting to compare Eq. (21) with Eq. (11). The displacement Q_0 of the center of the initial Gaussian distribution of the wave packet corresponds to the excitation of normal mode of the following quantum number:

$$\nu = \nu_c \tag{22}$$

where ν is related to Q_0 by Eq. (21.c). This relationship is in agreement with the corresponding relationship derived from the statistical analysis of the coherent state that the

contribution of excited state of normal vibration in the coherent state obeys the Poisson distribution.[49]

Thus, we have obtained the time-dependent aspect of the dynamic electron transfer and its relationship with the "additive" property.

III. DYNAMIC ELECTRON DENSITY

In order to elucidate the present theory, we shall demonstrate the results of numerical calculation of "dynamic electron density" of H_2, HD, HT, HF and HCl molecules and show the "additive" property. Since the systems are considered fairly "rigid", the operator Δ is neglected and the solution of Eq. (8) is used. We calculate dynamic electron density using ab initio molecular orbital methods. The ab initio calculations are done with Gaussian 80,[50] together with new subroutine to study the dynamic nature of electron density. The vibrational modes are calculated by HONDOG.[51] Basis set used in these calculations is 4-31G,[52] if not mentioned otherwise. The dynamic electron density $\langle\rho\rangle_0$ of H_2 molecule is depicted in Fig.1(a). Electron is localized at each nucleus symmetrically and distributed in the middle of the bond region. If the vibrational mode is excited, then the dynamic electron transfer occurs. Fig.2(a) shows the dynamic electron transfer of H_2 as the difference from the value of the dynamic

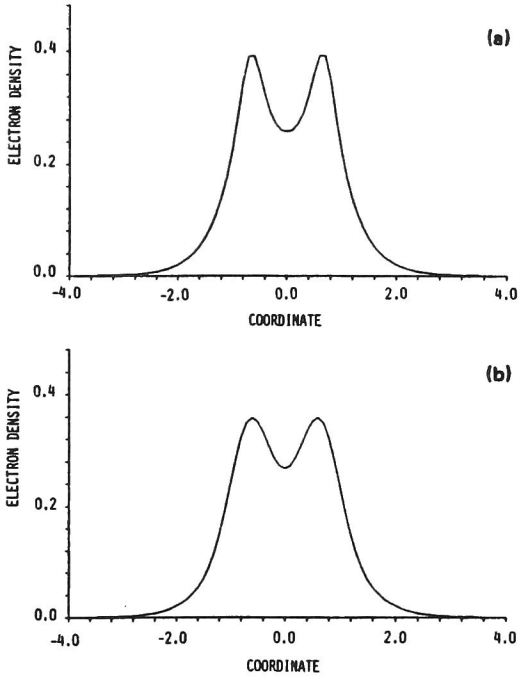

FIG. 1. Dynamic electron density $\langle \rho \rangle_0$ (in e/a.u.^{3}) of H_2 molecule is shown along the molecular axis. Two basis sets are used for the *ab initio* molecular orbital calculations: (a) 4-31G and (b) STO-3G. By using the 4-31G basis set, the equilibrium geometry and the vibrational frequency are determined. The nuclei in the equilibrium configuration are located at $\pm$ 0.6895 a.u. The vibrational frequency is 4650.8 cm^{-1}. Experimental values of equilibrium distance and vibrational frequency are 1.4016 a.u. and 4395.2 cm^{-1}, respectively (Ref. 57). All the STO-3G calculations in the present paper are performed by using the geometrical parameters of 4-31G calculations thus obtained.

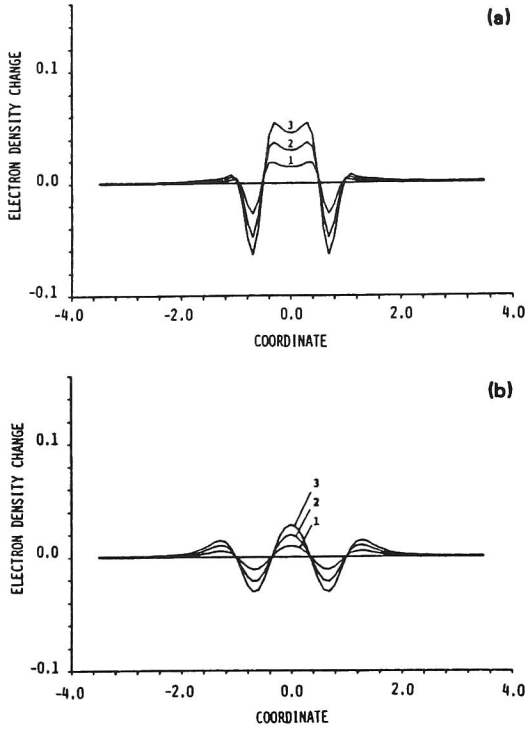

FIG. 2. Dynamic electron transfer $\langle \rho \rangle_v - \langle \rho \rangle_0$ of H_2 molecule along the molecular axis. The basis set dependence is shown in the same manner as in Fig. 1. The number in the figure denotes the vibrational quantum number: $v = 1,2,3$.

electron density corresponding to zero-point vibration. As the vibrational quantum number increases, dynamic electron transfer becomes large and clearly demonstrates the "additive" property predicted by Eq. (15).

The "additive" property represented here has some remarkable characters. First, the increment of electron density which accompanies the molecular vibration is proportional to the quantum number of molecular vibration. It should be noted that the experimental charge densities can be determined to an accuracy of about 0.005 $e \times au^{-3}$,[41] and the magnitude of the increment of electron density of H_2 induced by molecular vibration within the accuracy of our calculation is the order of $1 \times 10^{-2} e \times au^{-3}$. Hence, this additive property would be ascertained experimentally, for example, by mode-specific activation of molecular system, because this "additive" property is so fundamental and general.
Second, this "additive" property shows an expression of "quantization" of electron density and also gives some insight into a novel concept of the "dynamic structure" of molecular system. The dynamic molecular structure will be characterized by the nodal surfaces of the dynamic electron transfer. From the "additive" property, the dynamic molecular structure is independent of the quantum number of molecular vibration. And through these nodal surfaces a molecule exchange electrons inward and outward within it and with its environments as it

is vibrationally excited. As a special example of this electron exchange induced by molecular vibration, the dynamic electron transfer of H_2 is depicted in Fig. 2(a). The electron around a nucleus is transferred to both sides of the nucleus. The electron in the bond region is similarly transferred away but is compensated by the electron which is transferred from the terminal nuclei. Thus the "dynamic structure" of molecular system as the consequence of the "additive" property is clearly exhibited.

For the determination of the basis set dependence, the preliminary calculation performed with STO-3G basis set[53] are shown in Figs. 1(b) and 2(b). It is found that the qualitative feature of the dynamic electron transfer is the same as in the case of 4-31G basis set. Quantitatively, the dynamic electron transfer in the bond region is not so large as in the case of 4-31G basis set and electron which is transferred from the terminal nuclei completely compensates it.

Fig.3 shows the isotope effect of the dynamic electron transfer. As one of the terminal nuclei is replaced by heavier isotopes, D and T , the pattern of the dynamic electron transfer becomes asymmetrical. The heavier the terminal nucleus is, the smaller the dynamic electron transfer is; correspondingly, the heavier the terminal nuclei is, the larger the dynamic electron transfer is for the other terminal nucleus H. Also, there is another mass effect to the

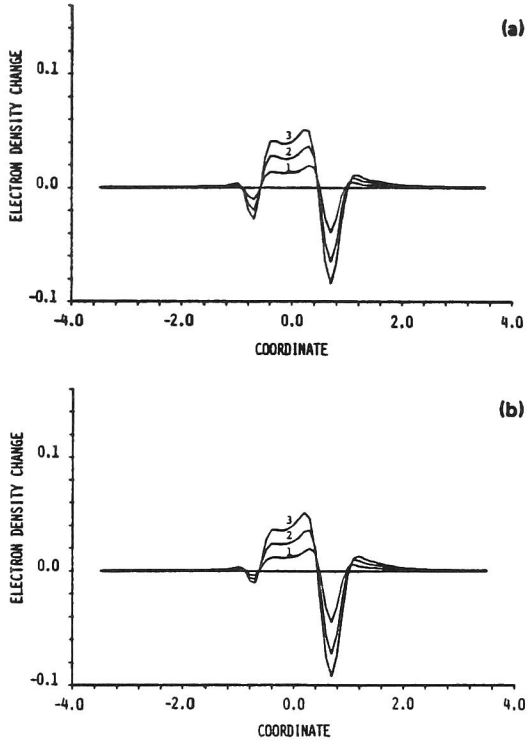

FIG. 3. Isotope effect of the dynamic electron transfer of (a) HD and (b) HT. The vibrational frequency is 4016.1 cm^{-1} for HD and 3781.0 cm^{-1} for HT. Experimental values of vibrational frequencies of HD and HT are 3817.1 and 3608.3 cm^{-1}, respectively (Ref. 57). The number in the figure denotes the vibrational quantum number: $v = 1,2,3$. As the left-hand side of the terminal nucleus is replaced by a heavier nucleus, the pattern of the dynamic electron transfer becomes asymmetrical.

"additive" property. As one of the terminal nuclei is replaced by heavier isotopes, the size of the dynamic molecular structural region shows the mass effect. For example, the region where the dynamic electron transfer has a negative value gets narrower at the side of the heavier isotope. Correspondingly, the region where the dynamic electron transfer has a negative value at the side of the lighter terminal nucleus H gets broader.

Figs. 4 and 5 show the dynamic total electron transfer and the contributions of the individual MOs for HF and HCl. MOs of HF and HCl are listed in Tables I and II. As is shown in the figures of total electron transfer, that is, Fig.4(a) for HF and Fig.5(a) for HCl, electron around nucleus is transferred to both sides of nucleus, and the magnitude of electron transfer is the largest at the neighborhood of F and Cl. This effect is attributed to the high electron density of core MOs, as is shown in Fig.4(b) for HF and in Fig.5(b)-(d) for HCl. The dynamic electron transfer on halogen nucleus itself shows negative value, which is not drawn in the figures because of the large singularity. The negative value of total electron transfer around F and Cl is the contribution mainly from the 2p- and 3p - orbitals of F and Cl, respectively, as is shown in Fig.4(d) for HF and in Fig.5(f) for HCl. These p-orbital effects are considered as the consequence of motion of p-orbital lobe density which accompanies molecular

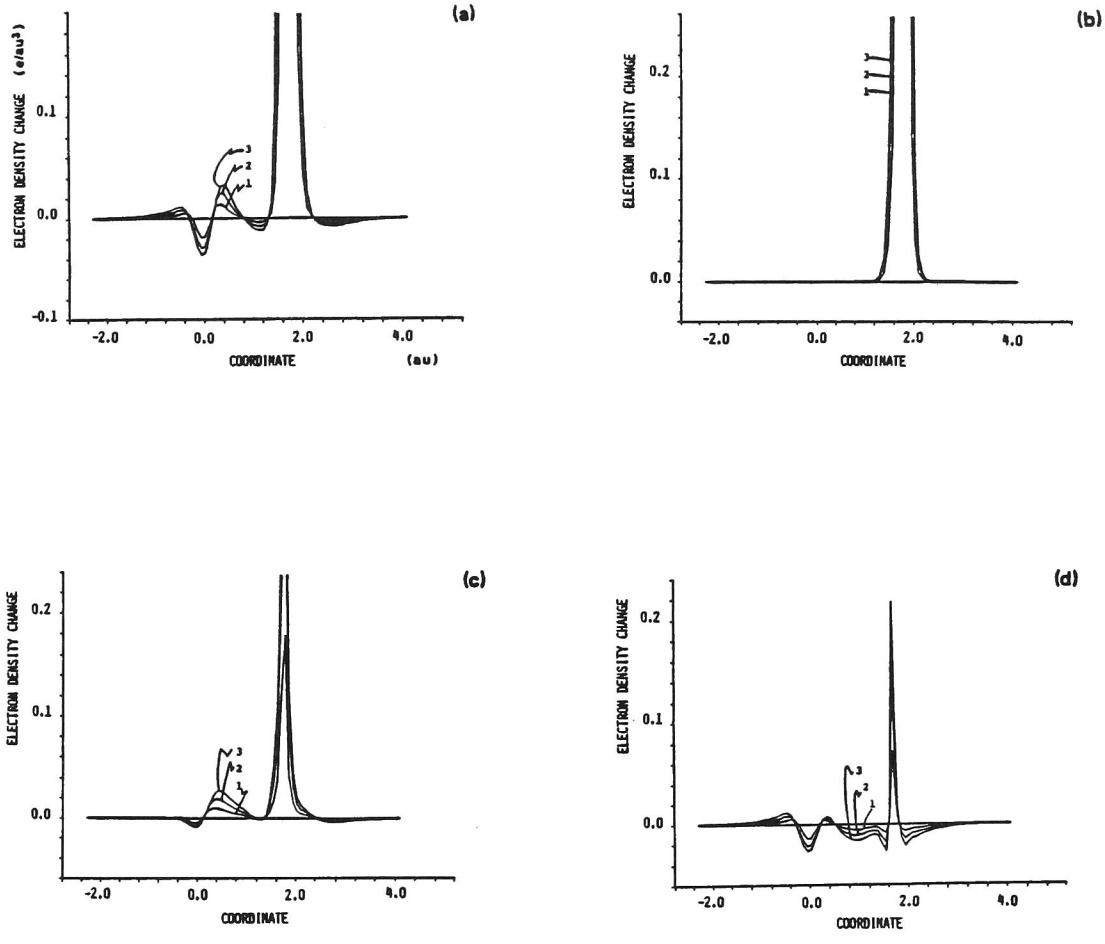

FIG. 4. Total dynamic electron transfer $\langle \rho \rangle_\nu - \langle \rho \rangle_0$ of HF molecule and contribution from individual molecular orbital to it. Total and contribution from $\phi_{HF(1)}$, $\phi_{HF(2)}$, and $\phi_{HF(3)}$ molecular orbitals are depicted in (a), (b), (c), and (d), respectively. Each molecular orbital is tabulated in Table I. Molecular orbitals which spread perpendicular to the molecular axis do not contribute to dynamic electron transfer on the molecular axis. The nuclei in the equilibrium configuration are located as follows: H at the origin, F at 1.7422, respectively. The vibrational frequency of HF is 4156.6 cm^{-1}. Experimental values of equilibrium distance and vibrational frequency are 1.7331 a.u. and 4138.5 cm^{-1}, respectively (Ref. 57). The number of the figure denotes the vibrational quantum number: $\nu = 1,2,3$.

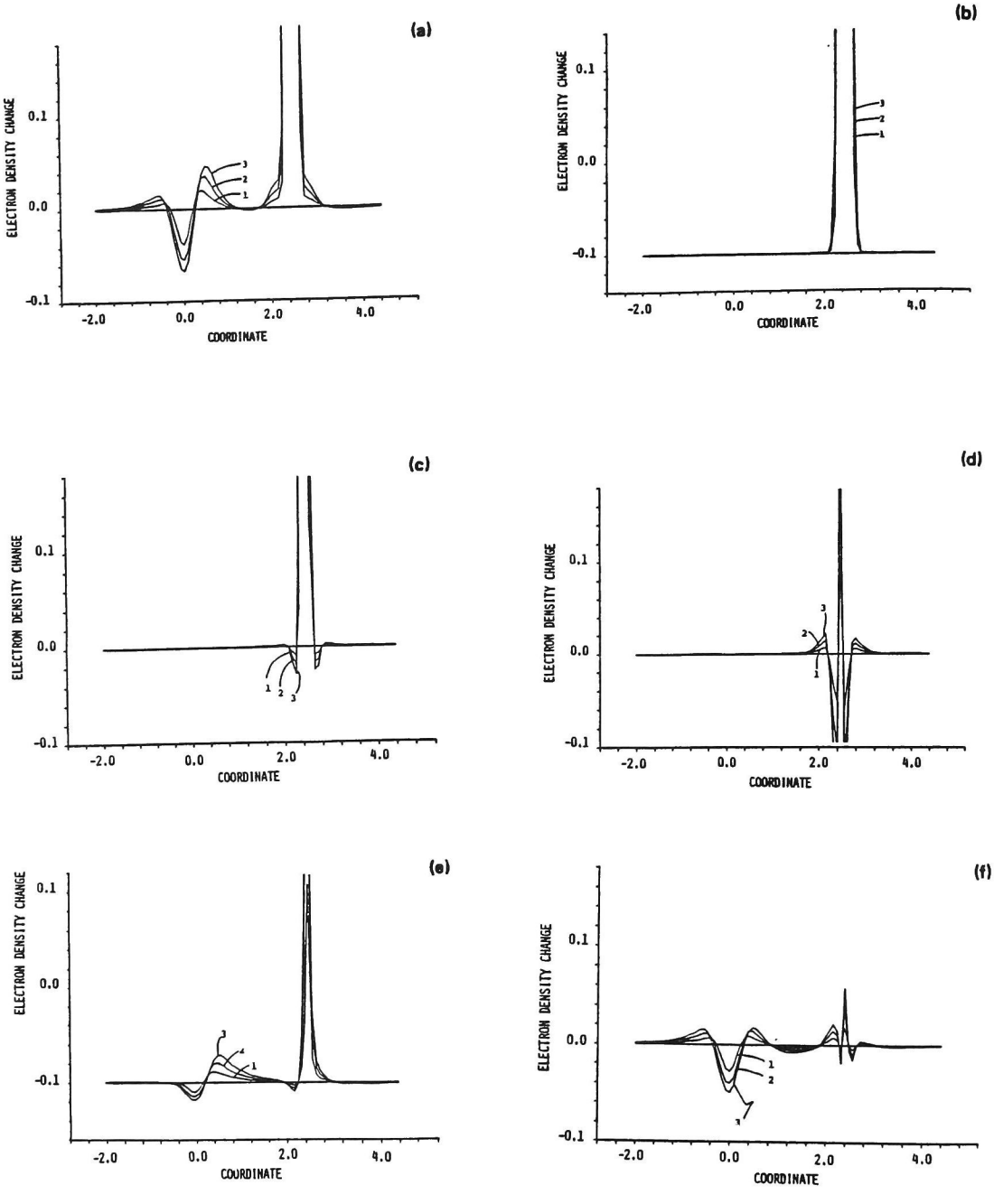

FIG. 5. Total dynamic electron transfer $\langle \rho \rangle_v - \langle \rho \rangle_0$ of HCl molecule and contribution from individual molecular orbital to it. Total and contribution from $\phi_{HCl(1)}$, $\phi_{HCl(2)}$, $\phi_{HCl(3)}$, $\phi_{HCl(6)}$, and $\phi_{HCl(7)}$ molecular orbitals are dipicted in (a), (b), (c), (d), (e), and (f), respectively. Each molecular orbital is tabulated in Table II. Molecular orbitals which spread perpendicular to the molecular axis do not contribute to dynamic electron transfer on the molecular axis. The nuclei in the equilibrium configuration are located as follows: H at the origin, Cl at 2.4539, respectively. The vibrational frequency of HCl is 2829.0 cm^{-1}. Experimental values of equilibrium distance and vibrational frequency are 2.4087 a.u. and 2989.7 cm^{-1}, respectively (Ref. 57). The number of the figure denotes the vibrational quantum number: $v = 1,2,3$.

TABLE I. Occupied MOs of the HF molecule. Two nuclei are located on the Z axis.

		$\psi_{HF(1)}$	$\psi_{HF(2)}$	$\psi_{HF(3)}$	$\psi_{HF(4)}$	$\psi_{HF(5)}$
H	$1S\,(I)$	− 0.000 99	− 0.129 09	− 0.291 87	0.0	0.0
	$1S\,(O)$	− 0.004 93	0.011 19	− 0.111 81	0.0	0.0
F	$1S$	− 0.991 05	0.229 15	− 0.061 41	0.0	0.0
	$2S\,(I)$	− 0.049 18	− 0.461 71	0.126 51	0.0	0.0
	$2Px\,(I)$	0.0	0.0	0.0	− 0.645 11	− 0.041 53
	$2Py\,(I)$	0.0	0.0	0.0	− 0.041 53	0.645 11
	$2Pz\,(I)$	0.001 97	0.080 53	0.534 96	0.0	0.0
	$2S\,(O)$	0.018 36	− 0.560 59	0.251 13	0.0	0.0
	$2Px\,(O)$	0.0	0.0	0.0	− 0.503 95	− 0.032 45
	$2Py\,(O)$	0.0	0.0	0.0	− 0.032 54	0.503 95
	$2Pz\,(O)$	− 0.003 28	0.050 07	0.364 01	0.0	0.0

TABLE II. Occupied MOs of the HCl molecule. Two nuclei are located on the Z axis.

		$\psi_{HCl(1)}$	$\psi_{HCl(2)}$	$\psi_{HCl(3)}$	$\psi_{HCl(4)}$	$\psi_{HCl(5)}$	$\psi_{HCl(6)}$	$\psi_{HCl(7)}$	$\psi_{HCl(8)}$	$\psi_{HCl(9)}$
H	$1S(I)$	− 0.000 22	0.000 86	0.001 46	0.0	0.0	0.152 20	− 0.295 63	0.0	0.0
	$1S(O)$	0.001 65	− 0.007 95	− 0.006 87	0.0	0.0	0.028 28	− 0.237 31	0.0	0.0
Cl	$1S$	− 0.991 54	0.285 32	− 0.003 67	0.0	0.0	0.081 36	0.026 41	0.0	0.0
	$2S$	− 0.028 96	− 1.021 45	0.012 30	0.0	0.0	− 0.336 47	− 0.117 69	0.0	0.0
	$2Px$	0.0	0.0	0.0	0.963 79	0.181 15	0.0	0.0	0.297 63	0.057 28
	$2Py$	0.0	0.0	0.0	0.181 15	− 0.963 79	0.0	0.0	0.057 28	− 0.267 63
	$2Pz$	0.000 15	0.011 17	0.979 51	0.0	0.0	0.044 04	− 0.219 15	0.0	0.0
	$3S\,(I)$	0.010 72	− 0.079 84	− 0.002 86	0.0	0.0	0.407 17	0.127 12	0.0	0.0
	$3Px\,(I)$	0.0	0.0	0.0	0.055 51	0.010 43	0.0	0.0	− 0.518 84	− 0.111 04
	$3Py\,(I)$	0.0	0.0	0.0	0.010 43	− 0.055 51	0.0	0.0	− 0.111 04	0.518 84
	$3Pz\,(I)$	− 0.000 36	0.003 50	0.060 08	0.0	0.0	− 0.081 57	0.420 36	0.0	0.0
	$3S\,(O)$	− 0.006 48	0.031 63	0.005 63	0.0	0.0	0.590 33	0.334 65	0.0	0.0
	$3Px\,(O)$	0.0	0.0	0.0	− 0.012 35	− 0.002 32	0.0	0.0	− 0.587 35	− 0.125 70
	$3Py\,(O)$	0.0	0.0	0.0	− 0.002 32	0.012 35	0.0	0.0	− 0.125 70	0.587 35
	$3Pz\,(O)$	0.001 05	− 0.005 53	− 0.017 12	0.0	0.0	− 0.055 55	0.347 79	0.0	0.0

vibration. The positive value of total electron transfer at the shoulder of H atom is originated from the 2s- and 3s - orbitals of F and Cl, respectively, as is shown in Fig.4(c) for HF and in Fig.5(e) for HCl. This interesting effect is interpreted as a delay of electron redistribution induced by molecular vibration and moreover, as the expression of a contribution from the ionic structure of HF and HCl, that is H^+F^- and H^+Cl^-. Deviations from the "additive" property can be seen at the bonding regions of HF and HCl molecules. These regions have the mobile electrons which travel with the lighter terminal nucleus H. Mathematically, the deviation from the "additive" property is due to the slow convergence of electron density ρ in terms of the Taylor series expansion with respect to the normal coordinate Q. That is, the quadratic expansion of ρ with respect to Q is not sufficient to describe the dynamic character. This means that electron density distribution ρ in Q-space spreads over the wide region. And this interpretation explain well the result that the deviation from the "additive" property is caused by the mobile electrons.

The time-dependent feature of the dynamic electron transfer of H_2 and HT molecules is depicted in Fig.6. The figure shows the results of calculation of Eq. (19) as the difference from the values of the dynamic electron density corresponding to the zero-point vibration .The minus(plus)

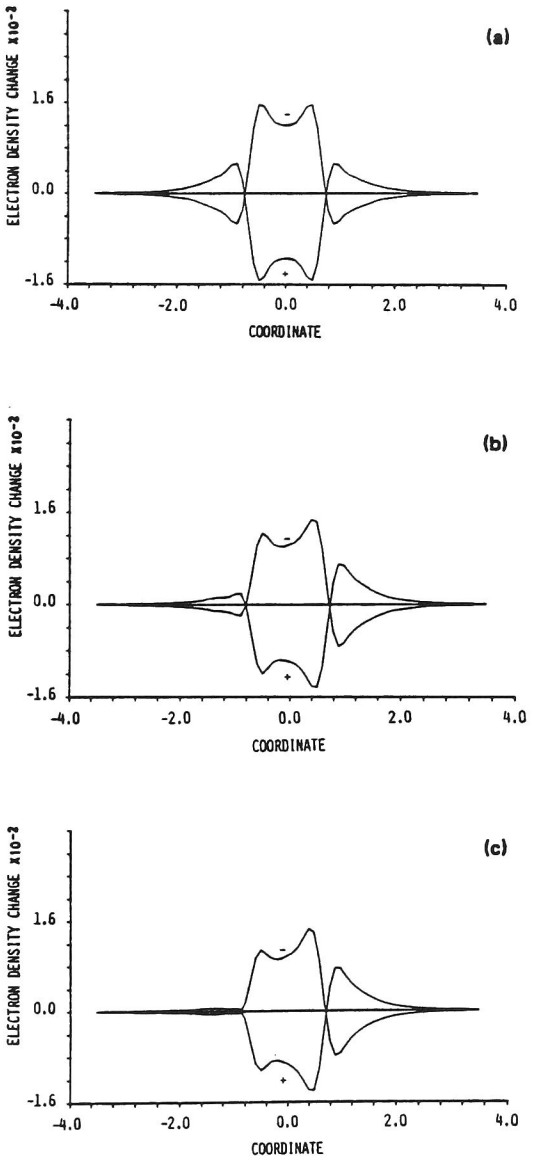

FIG. 6. Dynamic electron transfer $\langle \rho \rangle_{\text{coherent}} - \langle \rho \rangle_0$ of (a) H_2, (b) HD, and (c) HT molecules. We choose $Q_0 = 1.0$.

sign in the figure denotes the difference corresponding to the shortest (longest) bond length which appears during one period of vibration. As the bond length shortens, the electron is transferred from the outside of the bond region to the inside of the bond region, and vice versa. Now, the important relationship of Eq. (22) is available. Hence it is found that the present demonstration corresponds to excited vibrational states of ν_c= 19.31 for H2, ν_c=16.68 for HD, and ν_c=15.70 for HT. Similarly, the time-dependent feature of HF and HCl molecules is shown in Fig.7. The typical role of the p orbital of F and Cl are clearly exhibited. Using the important relationship of Eq. (22), the present demonstration is considered the excitation of ν_c=17.26 for HF and ν_c=11.75, for HCl.

Thus, the analysis of the dynamic electron density presents valuable information of the dynamic chemical nature of molecular system.

IV. CONCLUDING REMARKS

We have developed a method in order to understand the dynamic characters of electronic structure in the course of the internal motion of molecular system. First, we have proposed a new variational principle of the dynamic electron orbital. The dynamic effect of molecular vibration is

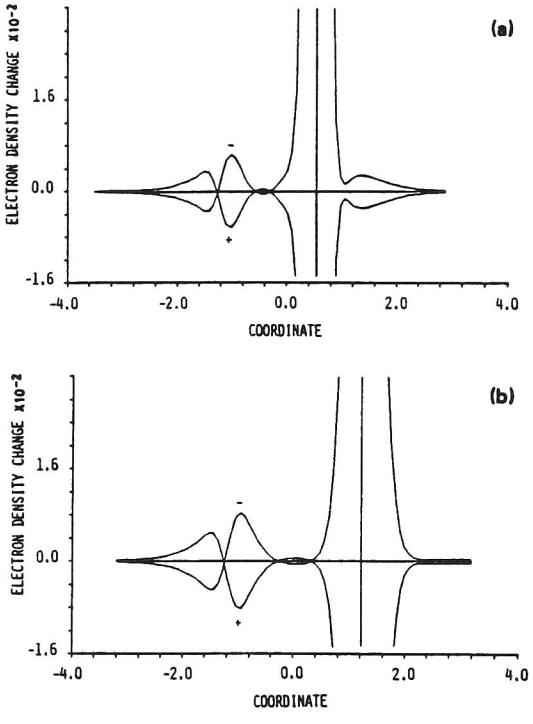

FIG. 7. Dynamic electron transfer $\langle \rho \rangle_{\text{coherent}} - \langle \rho \rangle_0$ of (a) HF and (b) HCl molecules. We choose $Q_0 = 1.0$.

incorporated into the electronic structure. Second, we have focussed our interest on the the dynamic electron density, and we have demonstrated the remarkable "additive" property of the dynamic electron density with respect to the vibrational quantum number. Time-dependent feature of the dynamic electron density is also analyzed on the basis of the coherent state, and an important relationship between the classical vibrational amplitude and the quantum number is obtained. The "additive" property of the dynamic electron transfer has been demonstrated numerically. In demonstrating the "additive" property, MO contributions have been analyzed to discuss dynamic chemical nature of molecules. This analysis is meaningful because MOs have played an important role in understanding chemical reactivity and bonding nature of molecules (for example frontier-orbital theory,[53] theory of the conservation of orbital symmetry,[54] and Bader-Pearson rules.[55]). These electronic structure theories have been applied to design the molecular properties and chemical reactivities. Therefore, it is interesting to develop the dynamic analysis of the electronic structure theory. Although the most rigorous approaches are fully vibronic ones, the analyses of the dynamic electron density give us the valuable informations, for example, the deformation of electronic density which accompanies the molecular vibration, and the dynamic contributions of the ionic structures in HF and HCl

molecules.

This development will enable us to understand and design the physical and chemical properties of the vibronic phenomena. This development will be achieved by utilizing the non-BO MO, which is proposed in this chapter, and this will be demonstrated in the future works. Furthermore, these analyses will give us new knowledge of physical and chemical nature of molecular systems. For example, the dynamic aspect of ring current model or the dynamic electronic states of aromatic molecule,[39] and investigation of the dynamic electronic process in chemical reaction dynamics are suitable applications of the present treatment. These applications are in progress and will be published elsewhere. But one remark should be referred to. To analyze chemical reaction dynamics, because of global character of potential energy hypersurface, one can not use harmonic approximation of vibrational motion, and hence we will utilize the "coherent dynamics".[11-14] This treatment has been developed by some authors, and considered to give promising results.

We think that the dynamic analysis of electronic structure gives us encouraging results and new insights with respect to chemical reaction dynamics, and it must be stressed that more dynamic treatments including non-BO framework toward the vibronic phenomena should be performed and more progresses in these fields are largely desired.

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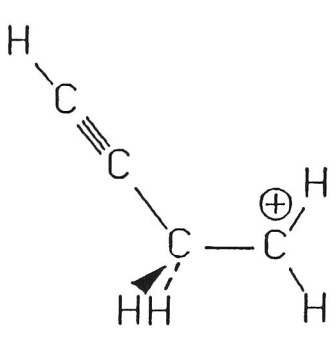
Chapter 4

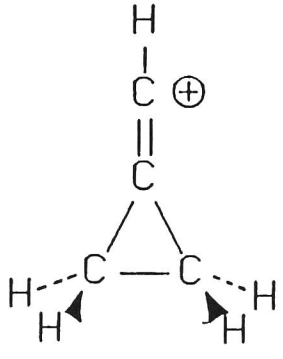
Theoretical Study on Carbocation with a Triple Bond

I. INTRODUCTION

The structures and stabilities of carbocations with an acetyl fragment are of considerable interest because there may or may not be participation of the triple bond in the cationic center in solvolytic reaction. The most sensitive factor of the reaction is the relative stability of geometrical isomers of cyclic and open forms. In the case of $C_4H_5^+$, it is considered to have three geometrical isomers, 1, 2, and 3.



1



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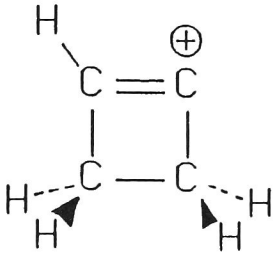
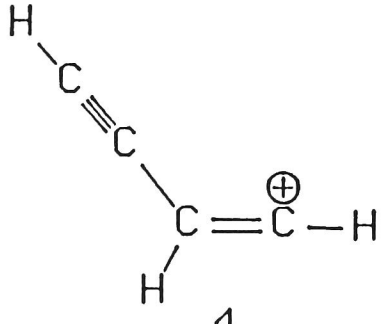


3

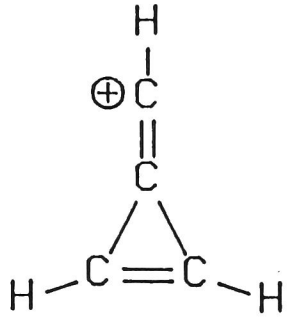
However, experimental studies in solution or gas phase do not directly predict the reaction mechanism or the geometry of the transition state. Therefore, many molecular orbital (MO) investigations have been performed in order to estimate the

stable geometries of intermediates and to analyze the solvolysis mechanism.[1] In this case, the three or four membered rings, 2 and 3, are ascertained to be the stable intermediates.

On the other hand, there are similar problems in vinyl cations.[2] The vinyl fragment may interact with substituents such as ethynyl, or phenyl groups and form a three membered ring. If a vinyl cation with an ethynyl group of the open form, 4, is given, it should be considered as having the geometrical isomer with a triangle in the molecule, 5.[3]



4



5

However, it is very difficult to make these cations because of their instability. Substitution with phenyl, anisyl etc. are essential for the formation of these kinds of carbocation. Experimental results suggest that the carbocation prefers an open structure, 4, over a triangular structure, 5.[4] On the other hand, in β-phenyl substituted vinyl cation of 4 the substituent is transferred and the more stabilized cation

formed reacts with the solvent.

The effect of the substitution group is rather sensitive in the formation of this type of carbocation. Therefore, it is very suggestive to calculate the substitution effect in the $C_4H_3^+$ cations with a methyl group as a substituent because it is possible to investigate the synthesizing of cyclo-compounds like 5 which have not yet been obtained.

The molecular vibration is closely related to the chemical reaction, because molecular vibrations result in the rearrangement of the electron distribution in the molecule. In the case of this carbocation, a specific vibration can promote the formation of the three-membered ring. Moreover, this effect probably relates to the stability of intermediates, i.e., ratio of the solvolysis products.

In this study, the unique reaction and geometries of $C_4H_3^+$ are investigated by use of *ab initio* MO calculations. The effect of molecular vibration on the formation of the cyclic intermediate is estimated by the use of the vibration-coupled electron density method.[4]

II. METHOD OF CALCULATION

MO's of carbocations were calculated by the use of the Gaussian80 program.[6] We used the 3-21G basis sets internal to the program for geometry optimization and the search for the

transition state. All geometries of molecules were optimized by use of the energy gradient method. The third-order Møller-Plesset correlation energies[7] are calculated for carbocations using 6-31G* basis sets and the optimized geometries of 4, the transition state and 5. Hereafter, theses energies are expressed by those with MP3/6-31G*//3-21G. Moreover, in order to ascertain the effect of the polrarization functions, 4 and 5 are optimized using 4-31G* basis sets and MP3/6-31G*//4-31G* energies are also estimated.

The vibration-coupled electron density can be estimated in the following manner,

$$<\rho>_n = \int \Phi_n^* \Phi_n \rho d\tau \qquad (1)$$

$$\Delta<\rho>_n = <\rho>_n - <\rho>_0 \qquad (2)$$

where Φ_n is the wave function of the nuclei and n indicates the quantum number of the vibration state. ρ is the density matrix of the electrons. The averaging of the electron density by the vibration wave function (eq. 1) can give us an estimate of the electron redistribution due to the excitation of the molecular vibration. $\Delta<\rho>_n$ is the difference between the ground and the excited state dynamic density and is called the dynamic electron transfer. This change of the electron density is caused by the excitation of a specific vibration mode.

III. RESULTS AND DISCUSSIONS

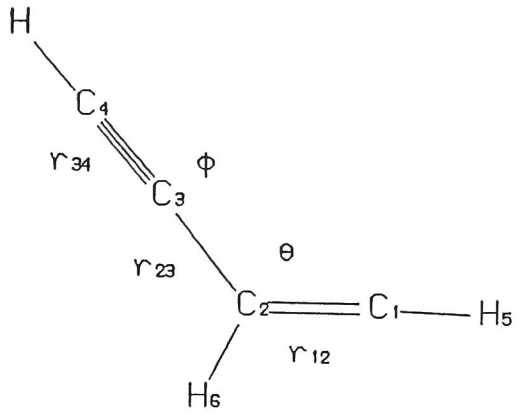
A. Geometry of the $C_4H_3^+$ Cation

Two possible geometries for C_4H_3+ are considered in this calculation.[3] One is an open chain form, **4**, and the other has a three membered ring, **5**. In addition, there also exists a transition state for the intra-conversion from **4** to **5** or vice versa. In order to determine these structures, geometry optimization and vibration analysis have been performed for these molecules using 3-21G basis sets. The optimized parameters for theses isomers are listed in Table I. Values in parentheses in the table are those using 4-31G* basis sets. The paramters for the open chain and triangular structures are depicted in Fig. 1. The calculated values for **4** do not indicate large difference between the two basis sets. However, those of **5** are considerably improved by the inclusion of polarization functions on the carbon atoms. The effect is important for the calculation of the cyclic geometry.

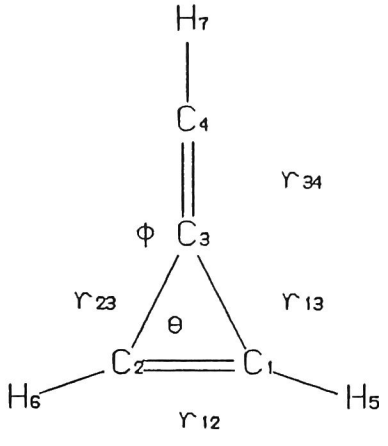
The total energies of **4** and **5** are calculated to be -151.90080 and -151.89288 Hartree, respectively. **4** is more stable by 5.0 kcal/mol than **5**. The geometry of the transition state of the reaction is also listed in the table and its total energy is -151.88833 Hartree. It lies higher by 7.8 kcal/mol than **4** and by 2.8 kcal/mol than **5**.

Table I Optimized parameters and total energies(+151 au) of $C_4H_3^+$ for geometries of 4, transiton state(TS), and 5 using 3-21G and 4-31G* (values in parentheses) basis sets.

		4	TS	5
r_{12}	(A)	1.279 (1.275)	1.258	1.266(1.267)
r_{13}		2.387 (2.411)	1.798	1.512(1.459)
r_{23}		1.409 (1.414)	1.476	1.512(1.459)
r_{34}		1.187 (1.183)	1.201	1.228(1.267)
θ	(deg)	114.9 (127.2)	81.7	47.9 (63.4)
ϕ		117.5 (181.5)	170.9	156.0(154.3)
T.E.	(au)	-0.90080	-0.88833	-0.89288
		(-1.60067)	-	(-1.61777)



(a)



(b)

Fig. 1. Geometrical parameters of C_4H_3+ with open chain (1a) and triangular (1b) structures.

However, 6-31G*//3-21G and MP3/6-31G*//3-21G energies give a different relative stability. For example, the latter energies are -153.23540 and -153.25960 Hartree for **4** and **5**, respectively. **5** is more stable by 15.1 kcal/mol than **4**. Moreover, the transition state obtained using the 3-21G basis set lies lower by 10.2 kcal/mol than **4** in MP3/6-31G*//3-21G* level calculations. This trend is also seen in 6-31G*//3-21G energies. These results are artificial because of not including the polarization function for carbon atoms. Therefore, it is necessary to optimize their geometries by use of larger basis sets with d-orbitals. In order to include this effect, geometries of **4** and **5** are optimized by use of 4-31G* basis sets. Total energies of **4** and **5** are -152.60067 (-153.23547) and -152.61777 (-153.25778) Hartree, respectively (values in parentheses are MP3/6-31G*//4-31G* energies). The relative stability of the two cations are consistent not with that of 3-21G but MP3/6-31G*//3-21G method. The transition state of intraconversion is also expected to be optimized by use of the larger basis sets. The activation energy for the cyclization using the 3-21G basis set is calculated to be 7.8 kcal/mol. On the other hand, inclusion of polarization functions and the correlation effect exchange the relative stability of the two cations. Therefore, the activation energy for the reaction is probably not so large.

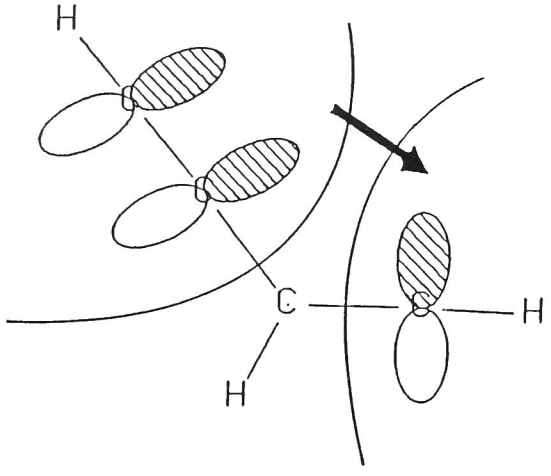
Although the quantitative properties such as total

energies or geometries require larger basis sets than the 3-21G one, the qualitative nature of the electron distribution, the shape of the MO, etc. are not so sensitive to the basis set difference. Therefore, we can use results obtained from the small basis sets for the latter discussions.

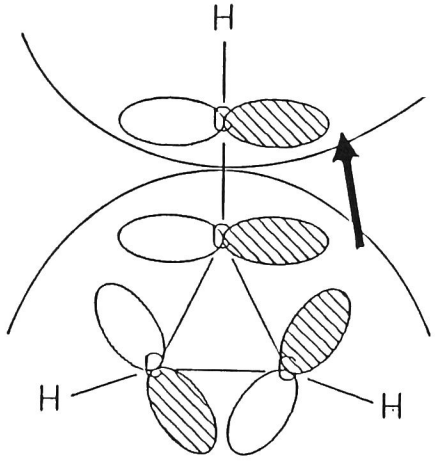
4 has suitable MO's for the formation of the three membered ring as illustrated in Fig. 2a. The occupied p orbital on the molecular plane transfers its electron density to the unoccupied p-orbital at the C_1 position. The electron transfer directly promotes formation of the C_1-C_3 bond. Calculated energies of these MO's are -0.623 and -0.220 Hartree, respectively. The facility of formation of the three membered ring is also increased by the vibration coupled electron density. This effect is discussed later.

Fig. 2b shows the interaction between the p-orbital at C_4 and the cyclopropene ring. This interaction causes the decrease of the anti-bonding character in the C_1-C_2 bond. Therefore, it is to be expected that the bond length in 5 is shorter than that in the $C_3H_3^+$. The calculated bond lengths in these molecules are 1.228 and 1.361 A, respectively.

The magnitude of the orbital interaction is closely related to the contribution of the resonance hybrid, 6.

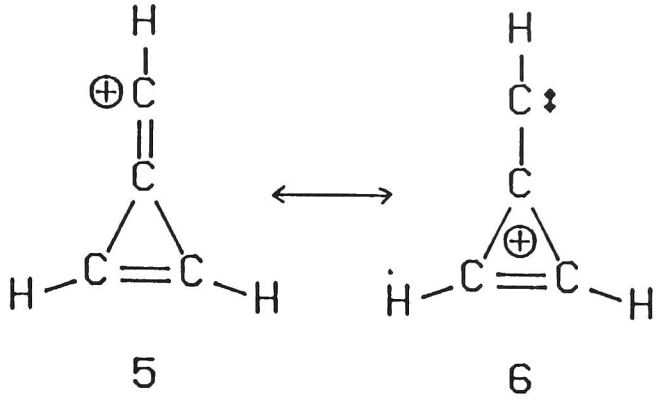


(a)



(b)

Fig. 2. Schematic representaion of orbital interactions between p- and π- orbitals (2a) and that between p- and Walsh orbital of cyclo-propenyl ring (2b).



5 6

It is necessary to accumulate electron density in the Walsh orbital of 5 in the unoccupied p-orbital at C_4 by the hyperconjugative interaction for the large carbene contribution. At the same time, the interaction stabilizes the cyclic cation as well as its derivatives.

On the other hand, this interaction causes an increase of the ring strain of the intermediate. The interaction, as well as the π bond in the perpendicular plane of the ring, leads to the considerably short C_1-C_3 bond calculated for 5 (1.228 Å), i.e., very large ring strain. This interaction does not work to stabilize the small ring structure. Therefore, the contribution of the resonance hybrid with a carbene is considered to be small for the $C_4H_3^+$ cation with the triangular geometry. Schleyer et al. pointed out that this interaction contributes largely to stability of 2. The similar interaction in these different cyclocompounds has a completely different role.

B. Relation between Ring Formation and Molecular Vibration

Molecular vibration causes redistribution of the electron density in molecules. It is pointed out that vibration modes of a molecule can be classified into two categories.[8] One is the system modes which relates a path of a specific reaction. The others are the so called "bath" modes which work as the energy lifting functions. The rearrangement of electron density due to excitation of a vibration mode, i.e., the dynamic electron transfer, can be calculated by use of eqs. 1 and 2. The excitation of a system mode causes the dynamic electron transfer which promotes the formation or dissociation of a chemical bond during a reaction. On the other hand, bath modes do not have such an effect. Therefore, it will be possible to relate the advance of a special reaction with the excitation of a specific vibration.

As mentioned above, interaction between the π-orbital in the ethynyl fragment and the unoccupied p-orbital at C_1 leads to the formation of the three membered ring. Therefore, the dynamic electron transfer due to the system mode will reveal an increase of the electron density between C_1 and C_3 atoms. Fig. 3 is a vibration mode calculated for the cation. The total dynamic electron transfer and its contribution of a p orbital induced by excitation of the mode are shown in Fig. 4a

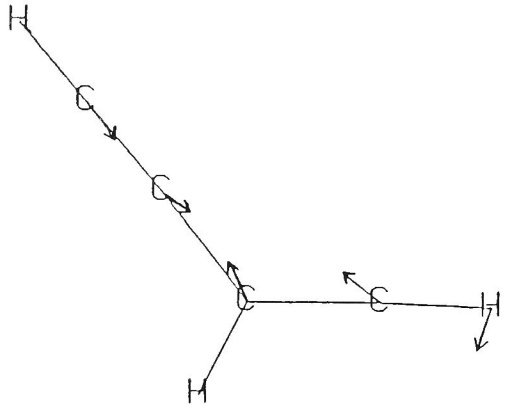


Fig. 3 The system mode for the reaction from 4 to 5. The dynamic electron transfers in Fig. 4 are calculated by use of this vibration mode.

and 4b, respectively.

Fig. 4a shows that increase of the electron density appears around the region in which the new C_1-C_3 bond is formed in cyclization. That is, the excitation of this mode leads to an increase of the density in the triangle. The rearrangement of the electron density is closely related to the formation of new bond. The dynamic electron transfer can be divided into the contributions of individual MO's. In this case, the π-p interaction is the most important and the occupied π orbital in the molecular plane is transferred to the unoccupied p orbital at C_4. Fig. 4b is the partial dynamic electron transfer due to the former orbital. As expected, this orbital largely contributes to the increase of the electron density in the triangle. Therefore, the vibration mode shown in Fig.3 is considered to be the system mode for the cyclization of a three membered ring.

C. Substitution Effect

As mentioned above, the cyclization of $C_4H_3^+$ is expected to occur easily. However, it is impossible to synthesize this cation because of its instability. On the other hand, substitution with electron releasing groups such as phenyl, anisyl or methyl groups gives stable derivatives of 4.

In order to get the stable structure of the δ-methyl substituted carbocation, **4a**, the geometry optimization was

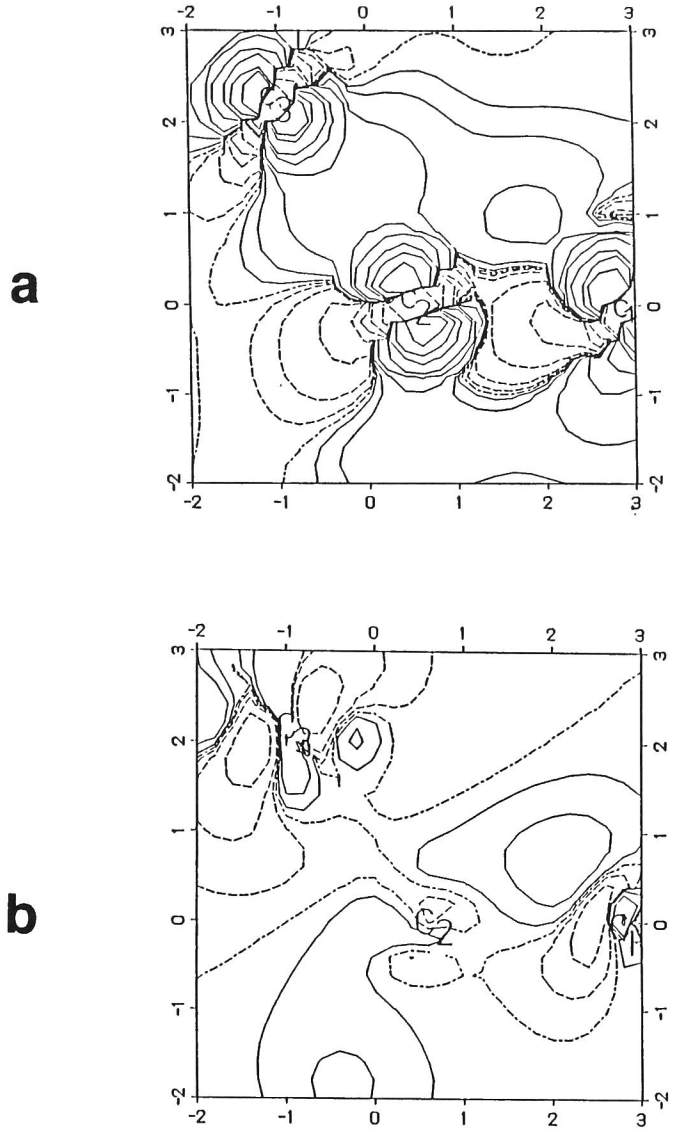
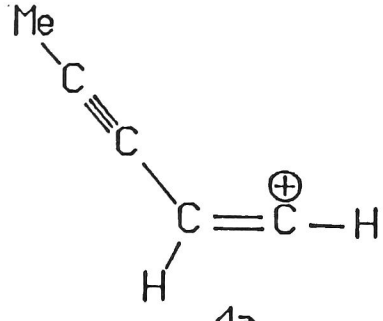
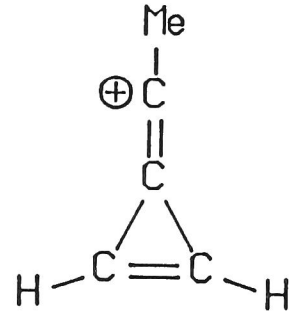


Fig. 4. The dynamic electron transfers $\Delta\langle\rho\rangle_3$ of $C_4H_3^+$. (4a) represents the total dynamic electron transfer and (4b) displays the partial one which is calculated by use of the π-orbital on the molecular plane. Solid, broken, and pecked lines indicate positive, null, and negative transfer, respectively. The values of the contours are ±0.01, ±0.003, ±0.001, ±0.0003, ±0.0001, ±0.00003, ±0.00001 for Fig. 4a and ±0.003, ±0.001, ±0.0003, ±0.0001 for Fig. 4b.

performed by use of the energy gradient method. When the initial geometry of **4a** is constructed by substituting the hydrogen atom, H_7, with a methyl group in the optimized open chain form, by a methyl group, the geometry with nearly the C_{2v} symmetry, **5a** is obtained. The results suggest that the triangular form is more stable than the open chain form. In the former geometry, the methyl group at the δ position in **4a** is attached to the α position of the cation center at C_4 in **5a**.



4a

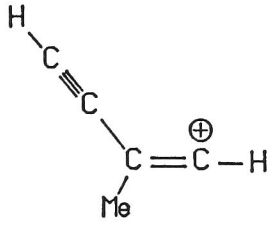


5a

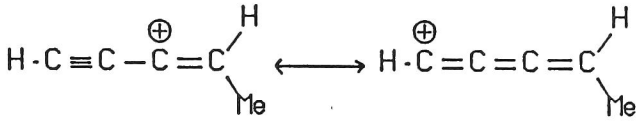
The methyl group in the molecule works as the electron releasing group. Therefore, substitution of a hydrogen atom by this group stabilizes the vinyl cation formed. The cation will prefer the geometry in which the methyl group is attached to the nearest position to the cation center, i.e., α position.

A similar trend is also calculated for the β-methyl substituted vinyl cation. In optimizing this molecule, the initial geometry is constructed by the replacement of H_6 in **4** by a methyl group. However, the optimized molecule is not **4b** but **7** in which the methyl group has rearranged its position

from C_2 to C_1.



4b



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These results indicate that the vinyl cation is apt to change its geometry in order to gain the more preferable interaction with the alkyl group when the methyl group is introduced at a position which is not the most favourable.

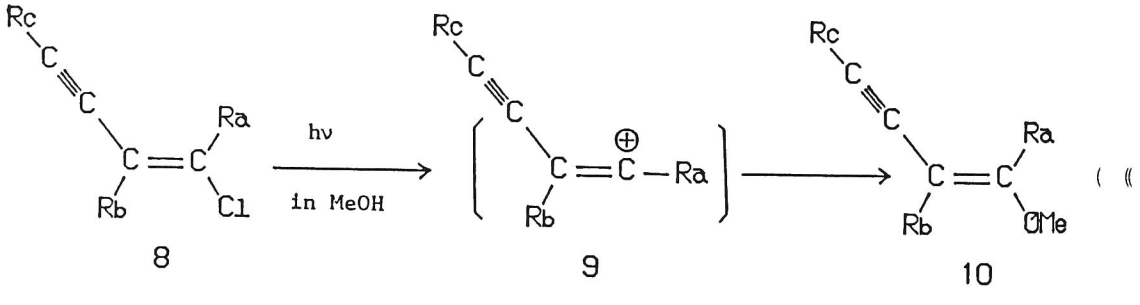
However, this trend cannot be generalized for other substituted vinyl cations because the calculated molecules have only one methyl group. It is necessary to substitute hydrogen atoms with phenyl, anisyl, or other electron releasing substituents in order to effect the solvolysis of vinyl cations with ethynyl fragment. The relative stability of the two geometrical isomers, triangular and open chain form , is largely affected by the kinds and positions of these substituents.

D. Comparison of Theoretical Expectations with Experimental

Results

From the synthetic view point, it would be very useful to prepare the derivatives of 5 but these have not been obtained yet. However, MO calculations suggest that it is very difficult to make these molecules because of the large ring strain in the molecule. In fact, there is little evidence that the resonance contribution, 6, is large.

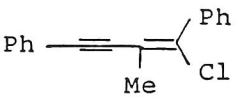
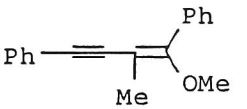
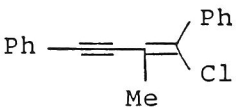
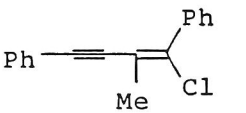
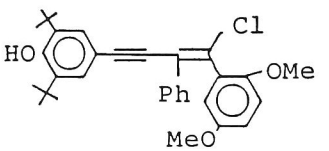
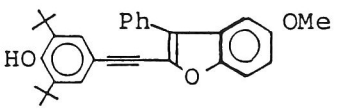
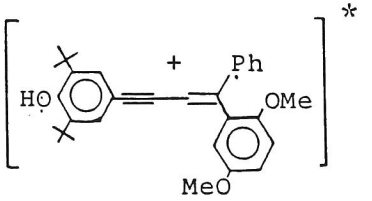
It is difficult to solvolyze vinylhalide in comparison with corresponding saturated halides. The difficulty arise from formation of the unstable cation. Therefore, it is necessary to substitute all of the hydrogen atoms with electron releasing groups in order to obtain vinyl cation derivatives.



8 9 10

Eq.3 shows photo-solvolysis of substituted vinyl halides and the products of the reaction are summarized in Table II.

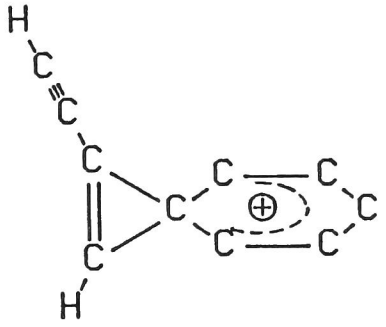
Table II Products of solvolysis of vinylhalides

Case	Reactant	Solvent	Main Product
A		MeOH	
B		CH_3CN	
C		THF	  *

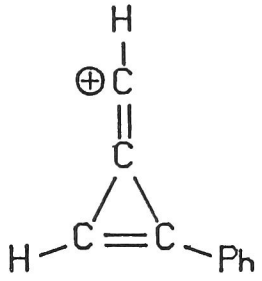
* The product was obtained through this carbocation

Geometrical isomers with Z- and E- structures are obtained as products. Therefore, the vinyl cation, **9**, is considered to exist in solution. Table II summarizes products of solvolysis for these derivatives. The α-substitution with phenyl group (R_α =ph) leads to the formation of the α substituted product with the solvent. The cation position is fixed by the introduction of a phenyl group. On the other hand, β-phenyl substitution causes the transfer of this group to a C_1 atom and, at the same time, the cation position moves from C_1 to C_2.

In the molecule with phenyl and ethynyl groups in the β-position, both of them are capable of interacting with the empty p-orbital at C_1. However, experimental results indicate the formation of a three membered ring between phenyl and vinyl fragments. The interaction between ethynyl and vinyl fragments is not favored for this molecule. While the spiro-interaction between a phenyl group and a π^*-orbital of the small ring fragment in **11** reduces the strain in the small ring, the effect does not exist in phenyl substituted cation, **12**. Therefore, the transfer of the phenyl group is more favorable than the formation of the small ring.



11



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IV. CONCLUDING REMARKS

Two geometrical isomers of C_4H_3+ are calculated to have similar stability. The activation energy for intra-conversion is rather small. Moreover, the analysis of dynamic electron transfer in $C_4H_3^+$ also predicts that the triangular isomer is easily formed from the open chain structure. However, experimental results suggest that the latter is much more stable than the former. The contradiction is due to the presence of substituents in the carbocation in which all the hydrogen atoms are replaced by electron releasing group such as phenyl, anisyl, and so on. For example, in β-phenyl cation (R_b=ph in 10), the formation of a three-membered ring between the phenyl and vinyl fragments is prefered over that between ethynyl and vinyl ones. Therefore, the β-phenyl substitution interferes with the formation of triangular forms like 4.

It is considered that there is only a small contribution from the carbene hybrid, 6. This is because this resonance

hybrid leads to short C_1-C_3 bond, i.e., very large ring strain. Therefore, it will be very difficult to synthesize derivatives which have a substituent introduced at the carbene carbon.

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[3] Two more geometrical isomers are considered to the C_4H_3 cation. They are $H_2C{=}C{=}C{=}C^+{-}H$ and the triangular pyramid structure. However, our attention is focussed only on the existence of the triangular isomers, **5**, and the intraconversion between **4** and **5**. Therefore, we calculated only **4**, **5** and transition state as the geometrical isomers of the C_4H_3 cation.

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Chapter 5

Conclusion

In part I of this thesis, the dynamic coupling of the electronic motions and the molecular vibration was studied.

In chapter 2 of this part, a general dynamic equation for an electron orbital is formulated for the dynamic study of the electronic motions coupled with the molecular vibration. The electron orbital obtained from this dynamic Fock equation reflects the effects of the kinetic energies of the nuclei and the quantum effects of the molecular vibration. If the energy exchange between the electronic motions and the nuclear motions is so small that one can regard it as a small perturbation, the zero-th order solutions will naturally be the adiabatic molecular orbitals. Then the orbital energy is the average of that of the adiabatic orbital over the nuclear motions.

The dynamic electron density in a molecular system, which reflects the quantum effect of molecular vibration, is analyzed. A novel additive property of the dynamic electron density with respect to the quantum number of the molecular vibration is found and proved. The characteristic change of the charge distribution of a H_2 molecule accompanying the excitation of a molecular vibration, which is named as the dynamic electron transfer, is analyzed to demonstrate the

additive property. The dynamic electron transfer of a cyclopropenyl cation accompanying the doubly degenerate molecular vibrations is also discussed to demonstrate a possibility of the vibrationally induced electron current. This may yield an interesting dynamic effect on the electron conductivity of the conjugated systems. The σ-electron participation in the ring current of an aromatic compound will also be discussed in a portion of chapter2 of part II.

In chapter 3 of this part, the general dynamic aspect of the electron density following the molecular vibration is investigated. A time dependent property of the dynamic electron density is analyzed on the basis of a coherent state of the nuclear motion. It is shown that the additive property of the dynamic electron density can be obtained again by taking a time average of the time dependent dynamic electron density over one period of the molecular vibration. Then an interesting relation between the amplitude of the coherently oscillating wavepacket and the quantum number of the molecular vibration is obtained. A thermal property of the electron density of the molecular system is also discussed using the vibrational temperature. The dynamic electron transfers of H_2, HD, and HT molecules are discussed to investigate the mass dependency of the dynamic electron transfer. It can be said that the dynamic electron transfer depends strongly on the atomic masses, and the transfer gets smaller when the atom is

replaced by its heavier isotope. The basis set dependency of the dynamic electron transfer is analyzed to ascertain how poor is the description given by a minimal basis set. The dynamic electron transfers and their orbital contributions in the HF and HCl molecules are investigated. An interesting feature is that the 2s orbitals of F and Cl atoms are concluded to have an important participation in the vibrationally induced ionic structure of the chemical bonding. The interesting density changes accompanying the motions of the lobe of the 2p orbital are obtained for the two molecules also. Finally, the time dependency of the dynamic electron transfer of these diatomic molecules is analyzed, which will be important in the nonstationary state of molecule.

In chapter 4 of this part, the isomerization reactivities and stabilities of the vinylcation with ethynyl fragment $C_4H_3^+$ in the two geometrical isomers open chain and triangular, are investigated to inquire into the possibility of the existence of the triangular isomer. The energetic stabilities and the barrier height of the isomerization reaction between the two isomers, calculated by the molecular orbital method, predict that both molecules are almost equally likely to exist. In spite of this, static analysis of the orbital interaction scheme favors the triangular form to be formed. In addition to this, the analysis of the dynamic electron transfer shows that the electron density is

accumulated in the region where the new bond of the triangular isomer is to be formed. The actual vinylcation molecule at a finite temperature would therefore favor the triangular form because, in that case, the effect of the molecular vibration cannot be neglected. The substitution effect alters this situation. The evidence from synthesis that the open chain form of this type of carbocation is favoured is ultimately due to the substitution effect.

Appendix to part I

On the Hartree-Fock Approximation to the Electronic Structure of Molecule in the Intense Radiation Field and the Strong Vibronic Coupling

The dynamic electronic structure of the molecular system has been studied in this part. The dynamic electronic structure studied does not take into account the background radiation field. The background radiation field is important in a vibronic system such as the ionic crystal system[1]. The polaron, the exciton, and the phonon are important elementary excitations in condensed matter physics[2] and the coupling between the molecular vibration and the electronic motion are important in their structure. Also the background radiation field, whose effect cannot be neglected, is implicit in them. Consequently it is interesting to investigate the vibronic coupling mechanism of a molecular system where the radiation field is coupled with the particle motion. A theory which is applicable for all wavelengths about the vibronic system exposed to a radiation field is awaited but it seems difficult to obtain a lucid theoretical framework. Here, the dynamic electronic structure of the molecular system which is influenced by the molecular vibration and the effect of the

infrared radiation field is investigated by generalizing the theoretical framework used in this part. The couplings among the electronic motion, the molecular vibration, and the intense radiation field can be studied by the coupled equations which will be derived in this appendix. These will be the fundamental equations for the nonlinear optical property of the molecular system.

Recently, the dressed molecular Hamiltonian[3] which includes explicitly the radiative correction in the molecular system has been studied by revising the Bloch-Nordsieck transformation used in the study of the radiative correction of an electron in the early days of quantum electrodynamics[4]. Then it will be interesting to apply the method which is used in this part to the dressed molecular Hamiltonian. The effect of the radiative correction as well as the molecular vibration can be incorporated into the one electron orbital.

The total Hamiltonian of the molecular system exposed in the radiation field within the minimal coupling[3,5] scheme is given as follows;

$$H_{TOT}=\sum_i (1/2m)\ \{p_i+(e/c)A(r_i)\}^2$$

$$+(1/2)\sum_{i,j}(e^2/r_{ij})-\sum_{\alpha,i}(Z_\alpha e^2/r_{i\alpha})$$

$$+\sum_\alpha (1/2M_\alpha)\ \{P_\alpha-(Z_\alpha e/c)A(R_\alpha)\}^2$$

$$+\sum_{\alpha,\beta}(Z_\alpha Z_\beta e^2/R_{\alpha\beta})$$

$$+(1/2)\int\{|\dot{A}(x)|^2+c^2|\nabla\times A(x)|^2\}dx^3, \quad (1)$$

where p_i , and r are the momentum and the coordinate of the electron whose mass and charge are denoted by m and -e, and P_α , and R_α are the momentum and the coordinate of the α-th nucleus whose mass and charge are denoted by M_α and $Z_\alpha e$, respectively. The speed of the light is denoted by c. The coulomb-guage[3,5] vector potential of the electromagnetic field $A(x)$ is given by the following Fourier transformed expression;

$$A(r,t)=V^{-1/2}\sum_{k,\lambda}\exp(ik\cdot r)\{\varepsilon_{k,\lambda}A_{k,\lambda}(t)+\varepsilon_{-k,\lambda}A_{-k,\lambda}^*(t)\}, \quad (2)$$

where $\varepsilon_{k,\lambda}$, $A_{k,\lambda}(t)$, and $A_{k,\lambda}^*(t)$ are one of the two independent polarization unit vectors for the transverse radiation with the wave vector k, the creation and the annihilation operators of the transverse radiation field with the wavevector k and the polarization λ, respectively. The quantization volume of the free field radiation is denoted by V. The dynamical variables of the quantized radiation field $P_{k,\lambda}$ and $Q_{k,\lambda}$ are defined as follows[3,5];

$$P_{k,\lambda}= |k|/(4\pi)^{1/2}[A_{k,\lambda}(t)+A_{k,\lambda}^*(t)], \quad (3)$$

$$Q_{k,\lambda}= i/c(4\pi)^{1/2}[A_{k,\lambda}(t)-A_{k,\lambda}^*(t)]. \quad (4)$$

In terms of the dynamical variables $P_{k,\lambda}$ and $Q_{k,\lambda}$, the vector potential $A(r,t)$ can be expressed as follows;

$$A(r,t)=2c(\pi/V)^{1/2}\sum\varepsilon_{k,\lambda}[\sin(k\cdot r)Q_{k,\lambda}$$

$$+\omega_k^{-1}\cos(k\cdot r)P_{k,\lambda}\Big]\,, \tag{5}$$

where ω_k denotes the frequency of the radiation mode **k** given by;

$$\omega_k=c\mid k\mid \tag{6}$$

Then the total Hamiltonian H_{TOT} is expressed as follows;

$$H_{TOT}=H_{mol}+H_{rad}+V_{int}\,, \tag{7.1}$$

$$H_{mol}=\sum_{\alpha}(1/2M_\alpha)P_\alpha^2+(1/2)\sum_{A,\beta}(Z_\alpha Z_\beta e^2/R_{\alpha\beta})+\sum_i(1/2m)p_i^2$$

$$+(1/2)\sum_{i,j}(e^2/r_{ij})-\sum_{\alpha,i}(Z_\alpha e^2/r_{i,\alpha})\,. \tag{7.2}$$

$$H_{rad}=(1/2)\sum_{k,\lambda}\{P_{k,\lambda}^2+\omega_k Q_{k,\lambda}^2\}\,, \tag{7.3}$$

$$V_{int}=(e/mc)\sum_i A(r)\cdot p_i-(e/c)\sum_\alpha(Z_\alpha/M_\alpha)A(R_\alpha)\cdot P_\alpha$$

$$+(e^2/2c^2)\{(1/m)\sum_i\mid A(r_i)\mid^2+\sum_\alpha(Z_\alpha/M_\alpha)\mid A(R_\alpha)\mid^2\}\,, \tag{7.4}$$

If the radiation field considered is limited to the infrared radiation, where the relations $k\cdot r_i\sim 0$ and $k\cdot R_\alpha\sim 0$ are satisfied for all the electrons and nuclei in the molecule, $A(r)$ can be approximated to be[3,5];

$$A(r,t)\sim 2c(\pi/V)^{1/2}\sum_{k,\lambda}\varepsilon_{k,\lambda}\omega_k^{-1}P_{k,\lambda}\,. \tag{8}$$

The interaction term between the radiation fields and the particles can be given as;

$$V_{int}=2e(\pi/V)^{1/2}\{(1/m)\sum_i p_i-\sum_\alpha(Z_\alpha/M_\alpha)P_\alpha\}\cdot\sum\varepsilon_{k,\lambda}\omega_k^{-1}P_{k,\lambda}$$

$$+2e^2(\pi/V)\{(1/m)+\sum_{\alpha}(Z_\alpha/M_\alpha)\}$$

$$\times\sum_{k,\lambda}\sum_{l,\eta}\varepsilon_{k,\lambda}\cdot\varepsilon_{l,\eta}(\omega_k\omega_l)^{-1}P_{k,\lambda}P_{l,\eta}, \tag{9}$$

where the second term of the right hand side of the equation denotes only the coupling between the two modes of the radiation field and does not affect the particle motion directly and hence it can be neglected, if the focus is put on the direct coupling of the particles and the radiation. Defining the unitary operator U;

$$U=\exp\Big[-2i(e/\hbar)(\pi/V)^{1/2}\sum_{k,\lambda}\omega_k^{-1}$$

$$\times\{\sum(1/m)\boldsymbol{p}_i-\sum_{\alpha}(Z_\alpha/M_\alpha)\boldsymbol{P}_\alpha\}\cdot\varepsilon_{k,\lambda}Q_{k,\lambda}\Big], \tag{10}$$

the dynamical variables are transformed as follows[3];

$$\acute{P}_{k,\lambda}=UP_{k,\lambda}U^{\dagger}$$
$$\sim P_{k,\lambda}+2e(\pi/V)^{1/2}\omega_k^{-1}$$
$$\times\{\sum(1/m)\boldsymbol{p}_i-\sum_{\alpha}(Z_\alpha/M_\alpha)\boldsymbol{P}_\alpha\}\cdot\varepsilon_{k,\lambda}, \tag{11.1}$$

$$\acute{Q}_{k,\lambda}=UQ_{k,\lambda}U^{\dagger}=Q_{k,\lambda}, \tag{11.2}$$

$$\acute{\boldsymbol{p}}_i=U\boldsymbol{p}_iU^{\dagger}=\boldsymbol{p}_i, \tag{11.3}$$

$$\acute{\boldsymbol{r}}_i=U\boldsymbol{r}_iU^{\dagger}$$
$$\sim\boldsymbol{r}_i-2(e/m)(\pi/V)^{1/2}\sum_{k,\lambda}\omega_k^{-1}Q_{k,\lambda}\varepsilon_{k,\lambda}, \tag{11.4}$$

$$\acute{\boldsymbol{P}}_\alpha=U\boldsymbol{P}_\alpha U^{\dagger}=\boldsymbol{P}_\alpha, \tag{11.5}$$

$$\acute{R}_\alpha = U R_\alpha U^\dagger$$

$$\sim R_\alpha + 2e(Z_\alpha/M_\alpha)(\pi/V)^{1/2}\sum_{k,\lambda}\omega_k^{-1}Q_{k,\lambda}\varepsilon_{k,\lambda}, \qquad (11.6)$$

where the linear expansion of the exponential operator is used. Using the transformed dynamical variables, the Hamiltonian is rewritten;

$$H_{rad}+V_{int}=(1/2)\sum\{\acute{P}_{k,\lambda}^2+\omega_k^2\acute{Q}_{k,\lambda}^2\}$$
$$-2e^2(\pi/V)\sum_{k,\lambda}\omega_k^{-2}\left[\{\sum_i(1/m)\acute{p}_i-\sum_\alpha(Z_\alpha/M_\alpha)\acute{P}_\alpha\}\cdot\varepsilon_{k,\lambda}\right], \qquad (12.1)$$

$$H_{mol}=\sum_\alpha(1/2M_\alpha)\acute{P}_\alpha^2+(1/2)\sum_{A,\beta}\{Z_\alpha Z_\beta e^2/(\acute{R}_{\alpha\beta}-\lambda_{\alpha\beta})\}$$

$$+\sum_i(1/2m)\acute{p}_i^2+(1/2)\sum_{i,j}(e^2/\acute{r}_{ij})$$

$$-\sum_{\alpha,i}\{Z_\alpha e^2/(\acute{r}_{i\alpha}-\xi_\alpha)\}, \qquad (12.2)$$

where $\acute{R}_{\alpha\beta}-\lambda_{\alpha\beta}$ and $\acute{r}_{i\alpha}-\zeta_\alpha$ are concretely given as follows[3];

$$\acute{R}_{\alpha\beta}-\lambda_{\alpha\beta}=|\acute{R}_\alpha-\acute{R}_\beta$$
$$-2e(\pi/V)^{1/2}\{(Z_\alpha/M_\alpha)-(Z_\beta/M_\beta)\}\sum_{k,\lambda}\omega_k^{-1}\acute{Q}_{k,\lambda}\varepsilon_{k,\lambda}|, \qquad (13.1)$$

$$\acute{r}_{i\alpha}-\xi_\alpha=|\acute{r}_i-\acute{R}_\alpha$$
$$+2e(\pi/V)^{1/2}\{(1/m)+(Z_\alpha/M_\alpha)\}\sum_{k,\lambda}\omega_k^{-1}\acute{Q}_{k,\lambda}\varepsilon_{k,\lambda}|, \qquad (13.2)$$

The Hamiltonian of the radiation field in terms of the transformed dynamical variables is obtained by substituting the transformed dynamical variables into the original

dynamical variables. The Hamiltonian of the molecular system is obtained through the substitution of the transformed dynamical variables into the original dynamical variables and the following replacement of the transformed nuclear coordinate;

$$\acute{R}_\alpha \rightarrow \acute{R}_\alpha - \Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\}), \tag{14.1}$$

$$\Delta R_\alpha(\{Q_{k,\lambda}\}) = 2e(\pi/V)^{1/2}\{(1/m)+(Z_\alpha/M_\alpha)\}\sum_{k,\lambda}\omega_k^{-1}\acute{Q}_{k,\lambda}\varepsilon_{k,\lambda}. \tag{14.2}$$

This replacement has the effect of modifying the Hamiltonian of the molecular system through the nuclear-electron and nuclear-nuclear coulomb potential. The dressed molecular Hamiltonian of the total system can be written as follows;

$$H_{TOT}=H_{rad}(\{\acute{P}_{k,\lambda},\acute{Q}_{k,\lambda}\}) + H_{mol}(\{\acute{p}_i,\acute{P}_\alpha,\acute{r}_i,\acute{R}_\alpha-\theta\sigma_\alpha\sum_{k,\lambda\&}\omega_k^{-1}\acute{Q}_{k,\lambda}\varepsilon_{k,\lambda}\})$$

$$-(1/2)\theta^2\sum_{k,\lambda}\omega_k^{-2}\left[\{\sum_i\acute{p}_i-\sum_\alpha(Z_\alpha/M_\alpha)\acute{P}_\alpha\}\cdot\varepsilon_{k,\lambda}\right], \tag{15}$$

where the substitution and the replacement are denoted symbolically, and where θ and σ_α are given by;

$$\theta=2e(\pi/V)^{1/2}, \tag{16.1}$$

$$\sigma_\alpha=\{(1/m)+(Z_\alpha/M_\alpha)\}. \tag{16.2}$$

The third term on the right hand side of Eq.(15) is corrected by the mass renormalization[4,5] correction and hence can be neglected. It is interesting to point out that the coupling

between the radiation field and the molecule is incorporated in the parametric dependence of the molecular Hamiltonian on the coordinate variable of the photon field. Then the situation resembles the vibronic problem of the molecular system.

Now with this dressed Hamiltonian[3], studied by Nguyen-Dang and Bandrauk, it is interesting to derive the electronic wavefunction which is suitable to describe the coupling between the radiation field and the particle motion of the molecule and the nonadiabatic coupling[6] between the nuclear motions and the electronic motions. Let the total wavefunction Ψ of the system be given by the following product;

$$\Psi=\Psi_e(\{\acute{p}_i,\acute{r}_i;\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})$$
$$\times\Psi_n(\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})\times\Psi_p(\{\acute{Q}_{k,\lambda}\}), \qquad (17)$$

where Ψ_e and Ψ_n are the electronic wavefunction and the nuclear wavefunction at the displaced nuclear configuration $\{\acute{r}_\alpha-\Delta\acute{R}(\{\acute{Q}_{k,\lambda}\})\}$, respectively. The photon eigenstate is denoted by Ψ_p. The right hand side of the semicolon in the brace denotes the parametric dependencies of the wavefunction. If the single Slater derterminantal electronic wavefunction constructed from the spin orbitals φ;

$$\varphi_i=\psi_i(\acute{r};\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})\theta, \qquad (18)$$

where ψ_i denotes the space orbital and θ the spin function, is adopted as Ψ_e, the electron orbitals coupled with the nuclear

motions and the radiation field are determined variationally, using the following energy functional;

$$E=\langle\Psi\mid H\mid\Psi\rangle$$
$$-\sum_{ij}\varepsilon_{ij}\langle\Psi_p\mid\langle\Psi_n\mid\langle\psi_i\mid\psi_j\rangle-\delta_{ij}\mid\Psi_n\rangle\mid\Psi_p\rangle$$

$$-\lambda(\langle\Psi_n\mid\Psi_n\rangle-1)-\eta(\langle\Psi_p\mid\Psi_p\rangle-1). \tag{19}$$

The electron orbitals $\{\psi_j\}$ are expanded in the basis set orbitals $\{\chi_k\}$;

$$\psi_j(\acute{r};\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})$$
$$=\sum_r c_{ri}\chi_r(\acute{r};\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\}), \tag{20}$$

where the basis set orbitals $\{\chi_r\}$ should satisfy the following orthonormalization condition;

$$\langle\Psi_p\mid\langle\Psi_n\mid\langle\chi_r\mid\chi_s\rangle\mid\Psi_n\rangle\mid\Psi_p\rangle=\delta_{rs}. \tag{21}$$

If the variation of the $\{c_{ri}\}$ is performed, the following Fock equation which determines the electron orbitals coupled with the nuclear motion and the radiation field can be written in atomic units as follows;

$$f=\langle\Psi_p(\{\acute{Q}_{k,\lambda}\})\mid\langle\Psi_n(\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{K,\lambda}\})\})\mid$$
$$\underline{F}+\underline{\Delta}\mid\Psi_n(\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})\rangle\mid\Psi_p(\{\acute{Q}_{k,\lambda}\})\rangle, \tag{22.1}$$

$$\Delta_{rs}(\{\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})=\sum_l\Big[(1/2)\langle\partial\chi_r/\partial\acute{Q}_l\mid\partial\chi_s/\partial\acute{Q}_l\rangle$$

$$+(1/2)\sum_j^{occ}\sum_{tu}c_{tj}^{*}c_{uj}^{*}\{\langle\partial\chi_r/\partial\acute{Q}_l\mid\chi_s\rangle\langle\chi_t\mid\partial\chi_u/\partial\acute{Q}_l\rangle$$

$$+\langle\partial\chi_t/\partial\acute{Q}_l\mid\chi_u\rangle\langle\chi_r\mid\partial\chi_s/\partial\acute{Q}_l\rangle$$

$$
\begin{aligned}
&-\langle \partial\chi_r/\partial\acute{Q}_l \mid \chi_u\rangle\langle \chi_t \mid \partial\chi_s/\partial\acute{Q}_l\rangle \\
&-\langle \partial\chi_t/\partial\acute{Q}_l \mid \chi_s\rangle\langle \chi_r \mid \partial\chi_u/\partial\acute{Q}_l\rangle\}\Big] \\
&+(1/2)\theta^2\sum_{k,\lambda}\sum_{\alpha\beta}\sigma_\alpha\sigma_\beta\omega_k^{-2}\Big[\langle \varepsilon_{k,\lambda}\cdot grad_\alpha\chi_r \mid \varepsilon_{k,\lambda}\cdot grad_\beta\chi_s\rangle \\
&+\sum_{j}^{occ}\sum_{tu} c_{tj}^{*}c_{uj}^{*} \\
&\{\ \langle \varepsilon_{k,\lambda}\cdot grad_\alpha\chi_r \mid \chi_s\rangle\langle \chi_t \mid \varepsilon_{k,\lambda}\cdot grad_\beta\chi_u\rangle \\
&+\langle \varepsilon_{k,\lambda}\cdot grad_\alpha\chi_t \mid \chi_u\rangle\langle \chi_r \mid \varepsilon_{k,\lambda}\cdot grad_B\chi_s\rangle \\
&-\langle \varepsilon_{k,\lambda}\cdot grad_\alpha\chi_r \mid \chi_u\rangle\langle \chi_t \mid \varepsilon_{k,\lambda}\cdot grad_\beta\chi_s\rangle \\
&-\langle \varepsilon_{k,\lambda}\cdot grad_\alpha\chi_t \mid \chi_s\rangle\langle \chi_r \mid \varepsilon_{k,\lambda}\cdot grad_\beta\chi_u\rangle\}\Big], \qquad (22.2)
\end{aligned}
$$

where the nuclear coordinates and the photon coordinate dependencies of the electronic wavefunctions are implicit in the right hand side of the Eq.(22.2), and where $grad_\alpha$ denotes $\partial/\partial\acute{R}_\alpha$. The collective coordinate of the l-th collective motion of nuclei is denoted by $\acute{Q}_l$. The usual Fock matrix at the nuclear configuration $\acute{R}_\alpha - \Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})$ is denoted by F in Eq.(22.1). The summation over l in Eq.(22.2) means that the summation is performed all over the modes of the nuclear collective motions. The nuclear wavefunction $\Psi_n\{\acute{R}_\alpha - \Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\}$ is determined by the following equation;

$$
\begin{aligned}
&\langle \Psi_p \mid \Big[-(1/2)\sum_l(\partial^2/\partial\acute{Q}_l^2)+(1/2)\sum_{\alpha\beta}\{(\dot{Z}_\alpha Z_\beta/(\acute{R}_{\alpha\beta}-\lambda_{\alpha\beta})\} \\
&+E^{el}(\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})+\sum_l D_l(\{\acute{R}_\alpha-\Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\})
\end{aligned}
$$

$$+\sum_{k,\lambda} D_{k,\lambda}(\{\hat{R}_\alpha - \Delta\hat{R}_\alpha(\{\hat{Q}_{k,\lambda}\})\}) - E\Big]\Psi_n \mid \Psi_p\rangle = 0, \tag{23}$$

where E^{el} is the electronic energy and where D_l and $D_{k,\lambda}$ are the nonadiabatic coupling energies between electronic motions and the l-th collective nuclear motions and between the electronic motions and the radiation field respectively;

$$D_l = \sum_{ij}^{occ} \{ \langle \partial\psi_j/\partial\hat{Q}_l \mid \partial\psi_j/\partial\hat{Q}_l \rangle$$

$$- \langle \partial\psi_j/\partial\hat{Q}_l \mid \psi_i \rangle \langle \psi_i \mid \partial\psi_j/\partial\hat{Q}_l \rangle \}, \tag{24.1}$$

$$D_{k,\lambda}$$

$$= \sum_{ij}^{occ} \sum_{k,\lambda} \sum_{\alpha\beta} \theta^2 \sigma_\alpha \sigma_\beta \omega_k^{-2} \{ \langle \varepsilon_{k,\lambda} \cdot grad_\alpha \psi_j \mid \varepsilon_{k,\lambda} \cdot grad_\beta \psi_j \rangle$$

$$- \langle \varepsilon_{k,\lambda} \cdot grad_\alpha \psi_j \mid \psi_i \rangle \langle \psi_i \mid \varepsilon_{k,\lambda} \cdot grad_\beta \psi_j \rangle \}. \tag{24.2}$$

The Eqs.(22) and (23) determine the electronic motion and the nuclear motion of the molecule exposed in the infrared radiation field where the nonadiabatic coupling between the electronic motion and the nuclear motion cannot be neglected and they will be the fundamental equations for the nonlinear optical property of the vibronic system.

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PART II

The Dynamic Electron Current Accompanying the Chemical Reaction

Chapter 1

Introduction

Recent developments in the laser chemistry enable one to investigate the detailed dynamics of the nuclear motion in a chemical reaction process from the microscopic standpoint. The energy transfer process in a chemical reaction system is studied both theoretically and experimentally. Especially, nonstatistical molecules in which the energy randomization process is strongly affected by the detailed dynamics of the nuclei are discussed actively. The anharmonicities including intermode couplings are important for the energy transfer process. The energy transfer process in an ideal chemical reacting system of a van der Waals molecule is studied experimentally and theoretically. The theoretical study of the van der Waals molecule is based on the rigid quantum mechanical method in the framework of neglecting the photon field.

In the theoretical study of the dynamics of polyatomic molecule, the consistent definition of the global coordinates which describe the dynamics efficiently is expected. Usually the reaction path Hamiltonian model which has an inconsistency in the most rigorous meaning is used. The Hamiltonian explains well the mode specific feature of chemical reactions. The system-bath decomposition of the reaction path Hamiltonian is

derived to discuss the essential dynamics of a chemical reacting system. The vibrational motions of the solvent molecules are a typical example of the bath modes which do not intervene in the reaction coordinate.

The theoretical study of the dynamics of nuclei including the nonadiabatic transition beyond the Landau-Zener scheme is performed actively in the framework of the wavepacket dynamics. The gas-solid interaction system is an interesting model for this kind of study. The other main problems where the dynamic coupling of the electronic motions and the molecular vibration plays an important role are, for example, the radiationless transition in the condensed phase, electron or proton transfer in biological systems, electron conductivity in organic and inorganic materials, and electronic structure of the nonrigid molecular system, such as Jahn-Teller effect and pseudorotation problem. The detailed study of the coupling between the electronic motions and the nuclear motions will be necessary for all these studies.

The study of the electronic process accompanying the dynamics of a molecule now relies completely on the clamped nuclei Born-Oppenheimer approximation. This is not satisfactory because it neglects the quantum effect of the nuclear motion even if the energy exchange between the motions of electrons and nuclei can be neglected. The dynamic electronic structure of a molecule which is influenced by the

quantum effect of the molecular vibration will enables us to present a new aspect of the molecular quantum physics of the chemical reaction.

In chapter 2 of this part (J. Mol. Struct. Theochem, 123,267(1985)), the dynamic spin and electron transfer accompanying a motion of a wavepacket along the IRC is studied for the radical reaction; $CH_3 + H_2 \rightarrow CH_4 + H$.

The dynamic electron density accompanying a motion of a wavepacket along the IRC converges to satisfy the rigid additive property at the stable equilibrium point of the potential energy surface. The mode specific feature of the vibrationally induced spin current is studied, and the interesting mode specificity is obtained. The difference between the current induced by the system and the bath mode vibrations are obviously represented. The isotopic effect on the current is also studied to elucidate the regular isotopic effect of the reaction observed by experiment. The participation of the dynamic α-electron and β-electron transfer to the spin current is analyzed also.

The dynamic electron transfer of the stable cyclopropenyl cation studied in this chapter is complementary to the discussion in a portion of chapter 2 of part I in this thesis. Here, the σ-, and π-electron participations in the vibrationally induced electron current are investigated to give a parallel discussion with the localized diamagnetic

current of the σ-electrons which is larger than that of the π-electrons in the ring current in the problem of the peculiar magnetic properties of aromatic compounds.

In chapter 3 of this part (to be submitted for publication), the coherent properties of the spin current induced by the quantum effect of the molecular vibration are investigated.

The directional vectors of the motions of the nuclei vary considerably in the course of large amplitude motion along the IRC. This is because of the nature of the curved space of the potential energy surface. The nature can be described using a methodology of the reaction ergodography. If the expansion coefficients of the displacement vector of the IRC are traced along the IRC by using the fixed basis vectors which are orthonormal and complete in 3N-dimensional mass-weighted space, the nature can be well explained. If the directional vectors of the translational and rotational motions and the normal vibrational vectors of the composite fragments in their stable structure are used to construct the fixed basis vectors of the chemical reacting system, the analysis is sustained by the physical intuition that will clarify how the nuclear motions of the composite fragments contribute to the intrinsic motions of the nuclei of the total chemical reacting system. It must be remembered that the IRC converges most probably to the weakest normal vibrational mode

at a stable equilibrium point of the potential energy surface. This stable limit theorem prefers a single kind of participation of the nuclear motions of the composite fragments at the stable point. In the collisional atom rearrangement reaction, the IRC will converge at the infinite stable equilibrium point to the translational motion which leads to a collision of the two composite fragments. It is interesting to investigate how this property of the nuclear motions affect the spin current induced by the quantum effect of the molecular vibration. The coherent property of the spin current is studied by expanding the spin current on the same footing with the expansion of the displacement vector of the IRC. The characteristic coherent properties of the spin current of the radical reaction; $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ are studied, whose dynamic electron current itself is studied in the chapter 3 of part III in this thesis. The vibrationally induced intermolecular interaction and its coherent property are also studied for this reaction. This is performed by calculating the dipole fluctuation of the two fragments within the supermolecular model and by examining how the quantum effect of the molecular vibration appears to induce the dipole fluctuation or not.

Finally, the conclusions obtained from chapter 2 to chapter 3 are discussed and summarized in chapter 4 of this part.

Chapter 2

Dynamic Electron Current Induced by Molecular Vibration

I. INTRODUCTION

Recently, the dynamical processes of molecular system have received much attention in the field of theoretical chemistry[1-2]. The stable feature of molecular system changes drastically through the onset of small perturbations[3-7], and the dynamical characteristics including the chaotic behaviour induced by anharmonicity[8] have been studied extensively in terms of nonlinear classical mechanics[9] and ergodic problem in fundamental statistical mechanics[6,10-11]. Moreover, quantum mechanical treatments have been applied to these problems in terms of the stability of state[12-16].

Experimentally, the intramolecular energy transfer process has received much interest in the study of the mode specific laser activation of molecule.[17-22] The possibility of the mode specific chemical reaction[17-21] is published in the light of this process. The intramolecular energy transfer process plays an important role also in the reaction system of biological molecules.

In the previous work[23], we have developed the dynamic analysis of electronic structure of molecule in the course of molecular vibration. The dynamics of molecular motion is incorporated into the electronic motion, and the dynamic electron orbital representing the nonadiabatic effect and the zero point vibrational effect to the electronic structure is obtained. The novel "additive" property of electron density which reflects the quantum effect of molecular vibration is demonstrated, and that this effect is fairly large enough to be observed by experimental study. Thus it is emphasized that the quantum effect of molecular vibration is largely reflected in the electron density distribution. Since the most rigorous treatment should be based on the full quantum mechanical description,[24-25] the above mentioned analysis provides us with novel concept of the dynamic electron transfer which accompanies the molecular vibration.

The topological structure of the electron density distribution itself has recently received much attention[26-29]. The deformation of the electron density distribution in the course of chemical reaction is clearly connected with the fundamental electronic processes which take part in the chemical bond scission and formation. The intrinsic property of the electron density on the electronic structure of atoms and molecules has been founded on the density functional theory of Hohenberg and Kohn[30-32].

In this chapter, we perform the analysis of the dynamic electron transfer in cyclopropenyl cation $C_3H_3^+$ and in a chemical reaction system $CH_3 + H_2 \rightarrow CH_4 + H$. In the former system, the character of electron current induced by molecular vibration is examined. In the latter system, the character of electron and spin currents in the course of chemical reaction is studied using a train of wavepackets. The center line of the train of wavepackets is the intrinsic reaction coordinate[33-35](IRC) of the reaction system. The electron current associated with the train of wavepackets along IRC converges to have the additive property at the stable point on the potential energy surface. This analysis enables us to study the electron transfer reaction dynamically which has been received much attention in the biological chemical reactions. For example, isotopic effect on the electron transfer process, and promoting and suppressing mode characterization of the reaction[36-38] can be investigated. The characterization of the vibrational mode in the course of the chemical reaction may be related with the mechanism of the intramolecular energy transfer process, and it will enable us to investigate the dynamics of the polyatomic chemical reactions.

II. METHOD OF CALCULATION

The details of the theoretical background have been published elsewhere[23], and hence the brief outline of the treatment will be shown in this section.

The dynamic electron density associated with the nuclear wavefunction Ψ_{nuc} is given as follows:

$$\langle \rho \rangle \equiv \int \rho \Psi_{nuc}^{*} \Psi_{nuc} dQ, \tag{1}$$

where ρ is the electron density distribution function which depends on nuclear coordinates and Q is a normal coordinate of molecular vibration. The dynamic electron density thus defined is also a natural consequence of the first order density matrix[39] of molecular wavefunction. If we adopt the harmonic oscillator wavefunction and if we expand ρ by Taylor series of Q, then we have the following additive property of the dynamic electron density,

$$\langle \rho \rangle_{nuc} \sim \rho(0) + (1/2\omega)(\partial^2 \rho / \partial Q^2)(0)(n+1/2) \tag{2}$$

where n is a vibrational quantum number of harmonic oscillator and ω is the frequency number of molecular vibration. The dynamic electron density given by the right hand side of Eq.(2) is linearly dependent on the vibrational quantum number. Then the change of the dynamic electron density are proportional to the difference of the vibrational quantum number Δn as the molecule is vibrationally excited. Especially if $\Delta n = 1$, the increment of dynamic electron density is $(1/2\omega)(\partial^2 \rho / \partial Q^2)(0)$. This term is propotional to the curvature of the electron density distribution function in the

Q-space, and if this curvature is positive(negative), the corresponding change of electron density at the point is positive(negative). We call the relationship of Eq.(2) the "additive" property, and we also call the electron density distribution change accompanying the excitation of the molecule the "dynamic electron transfer".

The analysis thus far mentioned is for the stationary state of a molecule, and it is necessary to introduce the parametrical motion to describe the non stationary process of the chemical reaction. Then we introduce the train of wavepackets along IRC which evolve as the reaction proceeds. The process of the evolution of wavepacket is schematically represented in Fig.1. The wavepacket is given as follows[40]

$$\Psi_{wavepacket} \equiv \Psi_{coherent}$$

where $\Psi_{coherent}$ is given by

$$\Psi_{coherent} = (\omega/\pi)^{1/4} \exp\{ -(1/2)\omega(Q - Q_0\cos\omega t)^2 - i\{(1/2)\omega t + \omega Q Q_0 \sin\omega t - (1/4)\omega Q_0^2 \sin 2\omega t\}\} \quad (3)$$

where Q_0 is an initial center of the gaussian wavepacket. By adopting $\Psi_{coherent}$ as the nuclear wavefunction Ψ_{nuc}, and expanding ρ by Taylor series of Q in Eq.(1), then we have the following dynamic electron transfer accompanying the coherent motion of nuclei along the reaction coordinate

$$\langle \rho \rangle_{wavepacket} \sim \rho(s) + (\partial\rho/\partial Q)(s) Q_0 \cos\omega t + (1/2)(\partial^2/\partial Q^2)(s)\{1/(2\omega) + (Q_0\cos\omega t)^2\} \quad (4)$$

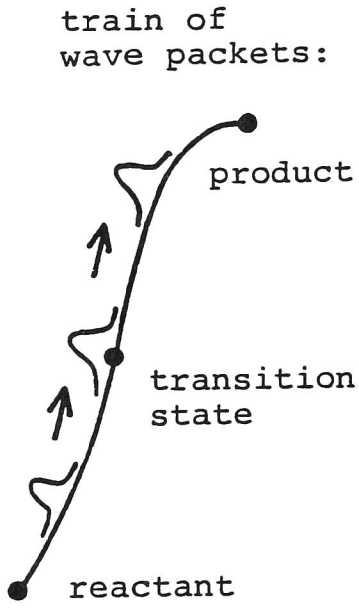

Fig. 1. Schematic representation of the train of wave packets along the reaction coordinate.

where s is the IRC. If we take the average of $\langle\rho\rangle_{wavepacket}$ over one period τ at the stable point, then we have

$$\overline{\langle\rho\rangle}_{wavepacket} \equiv (1/\tau)\int_0^\tau \langle\rho\rangle_{wavepacket} dt$$

$$\sim \rho(0) + (1/2\omega)(\partial^2\rho/\partial Q^2)(0)(n_c + 1/2) \quad (5)$$

where τ is given by $2\pi/\omega$ and n_c is represented by

$$n_c = (1/2)\omega Q_0^2 \quad (6)$$

If we correlate the n_c with the quantum number n of Eq.(2), then the dynamic electron transfer accompanying the train of wavepackets on the reaction coordinate converges to satisfy the rigid additive property at the stable point.

All the calculations are performed at the UHF[41] 4-31G[42] level. We use HONDOG program[43] to calculate the normal vibrational modes and the reaction coordinate. We also use Gaussian 80 program[44] which is modified to calculate Eq.(1) numerically.

III. DYNAMIC ELECTRON TRANSFER

A. Cyclopropenyl Cation

Recent investigations of aromatic compounds shed a new light on the ring current model of the peculiar magnetic properties[45,46]. The paramount importance of localized

diamagnetic current of σ electrons over that of π electrons has been revealed. We shall choose the smallest aromatic compound, the cyclopropenyl cation, and examine the dynamic electron current induced by the in-plane molecular vibration.

The static distribution of electron density ρ is shown in Fig.2. The ρ is decomposed into the contributions of σ and π electrons:

$$\rho=\rho_\sigma+\rho_\pi \tag{7}$$

According to Fig.2(a), the distribution of the σ-electron density ρ_σ demonstrates the bent C-C bond of the system; this is in close agreement with the contour diagram of valence electron density drawn in the molecular plane[47]. It should be noted that the σ-electron deficient region is found in the center of the system and above position of carbon nucleus. On the other hand, according to Fig.2(b), the distribution of the π-electron density ρ_π clearly shows the typical pattern of the $2p\pi$ lobe centered on carbon nucleus. The sum of ρ_σ and ρ_π is depicted in Fig.2(c). The large contribution of ρ_σ is remarkable.

The cyclopropenyl cation has the doubly degenerate vibrational modes in the molecular plane. The schematic pictures of the vibrational modes ν_1 and ν_2 are shown in Figs.3(a) and 3(b) , respectively. These vibrational modes are coupled to yield the angular momentum which is perpendicular to the molecular plane[48], as shown in Fig.3(c). If such

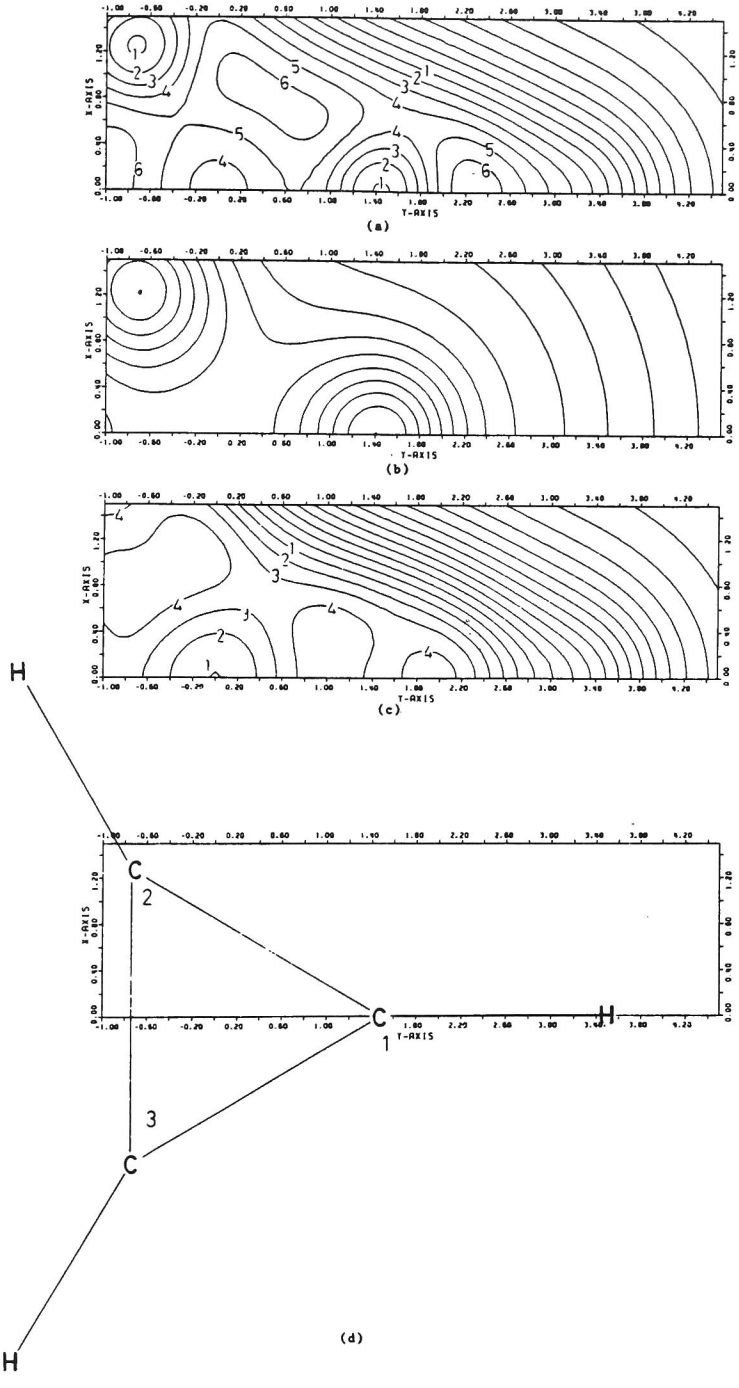

Fig. 2. Contour maps of the static electron densities of the cyclopropenyl cation in a parallel plane 0.8 a.u. over the molecular plane: (a) σ-electron, (b) π-electron and (c) total electron. (d) Key of the figures drawn throughout this paper. The nuclei in the equilibrium configuration drawn in the contour maps are located, from left to right, at C(1.286, −0.742), C(0.0, 1.485), and H(0.0, 3.405), respectively. The unit of coordinate is a.u. The contours are drawn as follows. (a) From 0.01 to 0.18 with an increment of 0.01. Indices mean 1 = 0.09, 2 = 0.10, 3 = 0.11, 4 = 0.12, 5 = 0.13, and 6 = 0.14. (b) 0.0001, 0.0003, 0.001, 0.003, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, and 0.09. (c) From 0.01 to 0.18 with an increment of 0.01. Indices mean 1 = 0.15, 2 = 0.16, 3 = 0.17, and 4 = 0.18. The unit of electron density is e/a.u^3.

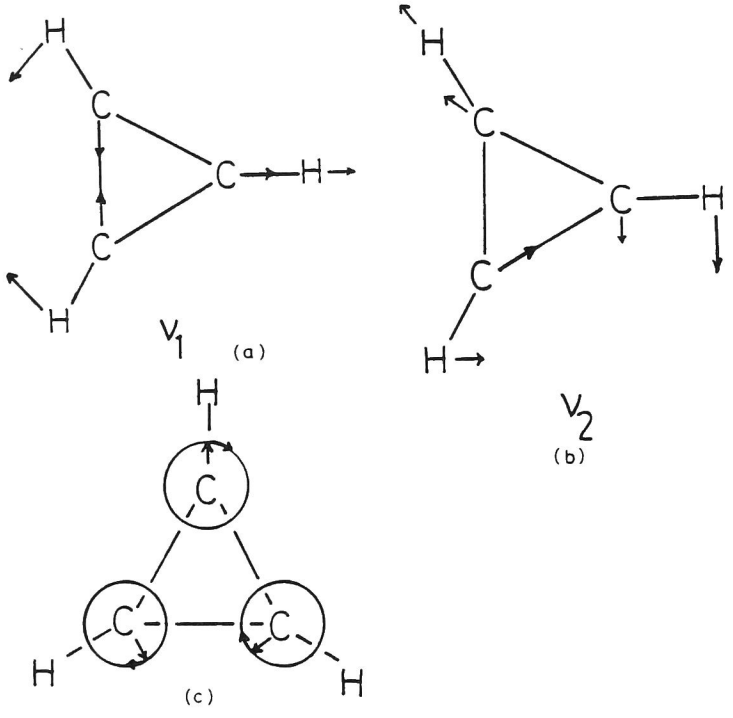

Fig. 3. Schematic views of the in-plane normal vibrational modes: (a) ν_1 mode, and (b) ν_2 mode. Both modes have the vibrational frequency 1038 cm^{-1}, and are degenerate with each other. (c) These modes are coupled to yield the angular momentum which is perpendicular to the molecular plane, as shown in this figure.

mode-specific excitation of molecular vibration is designed, then it is expected that the dynamic electron current which has non-zero angular momentum may be induced. This may give a characteristic dynamic effect on the σ-electron participation in the ring current model of aromatic compounds[23].

The characteristic features of the dynamic electron transfer induced by the modes ν_1 and ν_2 are shown in Figs.4-6 and Figs.7-9, respectively. The dynamic electron transfer is analyzed here by the increment of the electron current as follows:

$$\langle\rho\rangle_n - \langle\rho\rangle_0 \ ; \ n=1,2,3. \qquad (8)$$

As the vibrational mode is excited from the zero-point energy level to higher order energy levels, the additive dynamic eletctron transfer occurs. This is predicted by Eq.(2), and is clearly shown in Figs.4-9. Indeed, the nodal line which represents the locus of null transfer remains unchanged during the course of excitation. According to Figs.4-9, the σ-electron transfer is predominant over the π-electron transfer. The two-dimensional pattern of the dynamic electron current is almost represented by that of σ-electron current. The accumulation of the electron density inside of the ring is typical. The electron density which accumulates inside of the ring considerably oozes through the C-C bond. It should be noted that the local nature of the electron density distribution on carbon is characteristic of the present

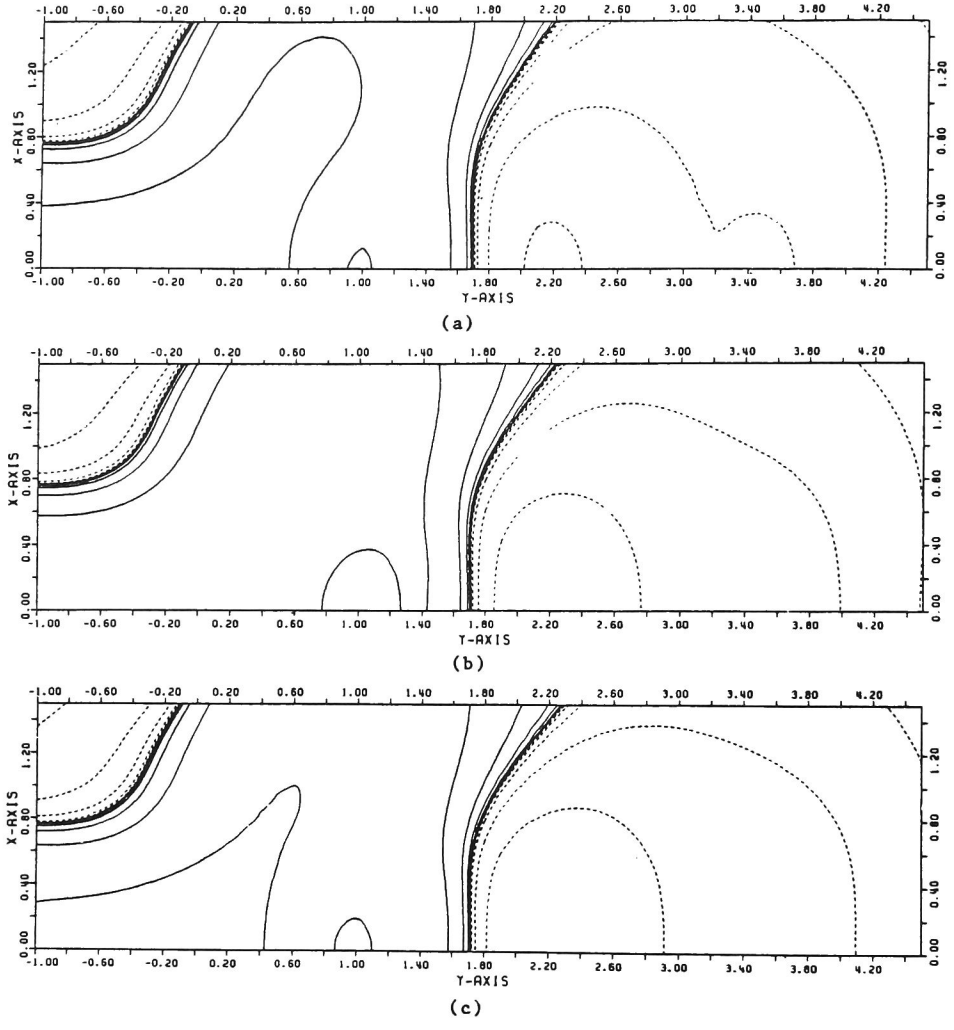

Fig. 4. Dynamic σ-electron transfer $\langle\rho\rangle_n - \langle\rho\rangle_0$ induced by mode ν_1 in a parallel plane 0.8 a.u. over the molecular plane: (a) $n = 1$, (b) $n = 2$, and (c) $n = 3$. Solid line and dotted line correspond to increase and decrease of the dynamic electron transfer, respectively. The broken line shows null transfer. The values of the contours are $\pm 1.0 \times 10^{-n}$ $\pm 3.0 \times 10^{-n}$, and 0.0 (n = 4, 5, 6). In (c), $\pm 1.0 \times 10^{-3}$ are added.

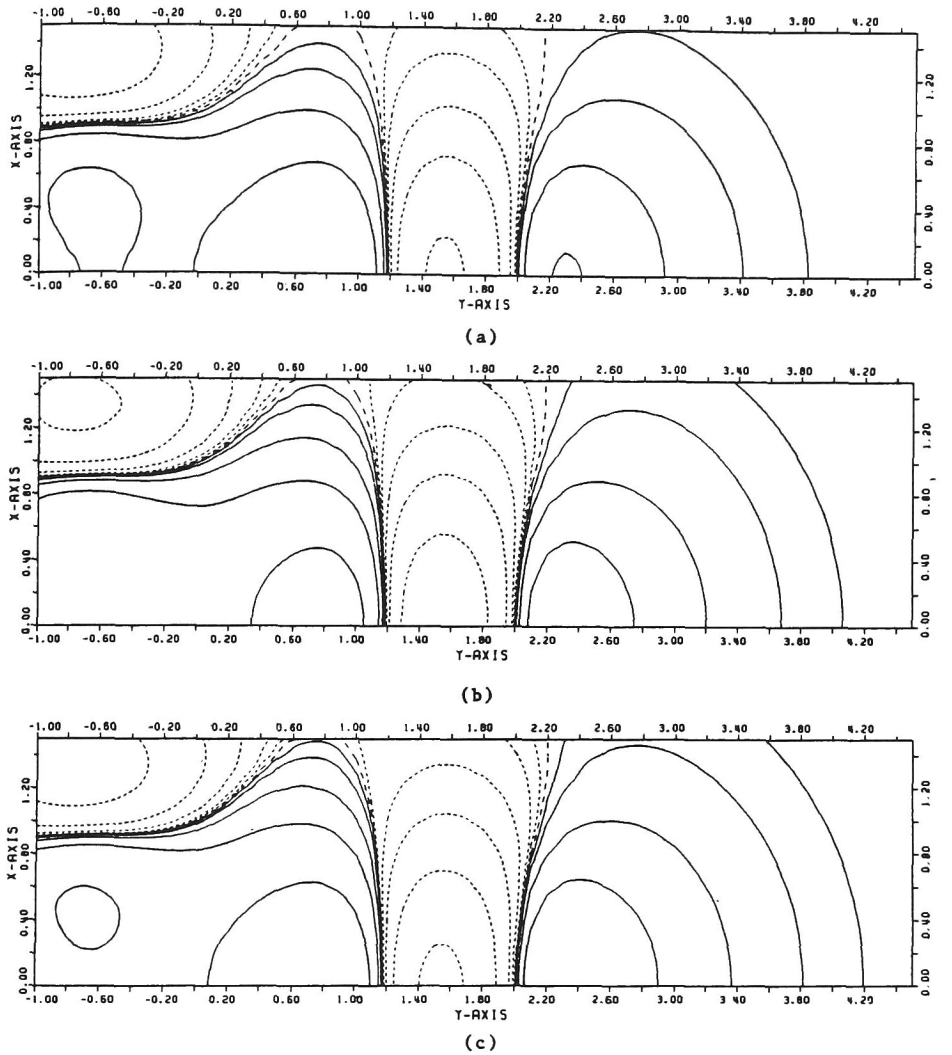

Fig. 5. Dynamic π-electron transfer induced by mode ν_1. The meaning of the figure is the same as in Fig. 4. The values of the contours are $\pm 1.0 \times 10^{-n}$ (n = 4, 5, 6), $\pm 3.0 \times 10^{-n}$ (n = 5, 6), and 0.0; 1.0×10^{-4} is omitted in (a), and 3.0×10^{-4} is added in (c).

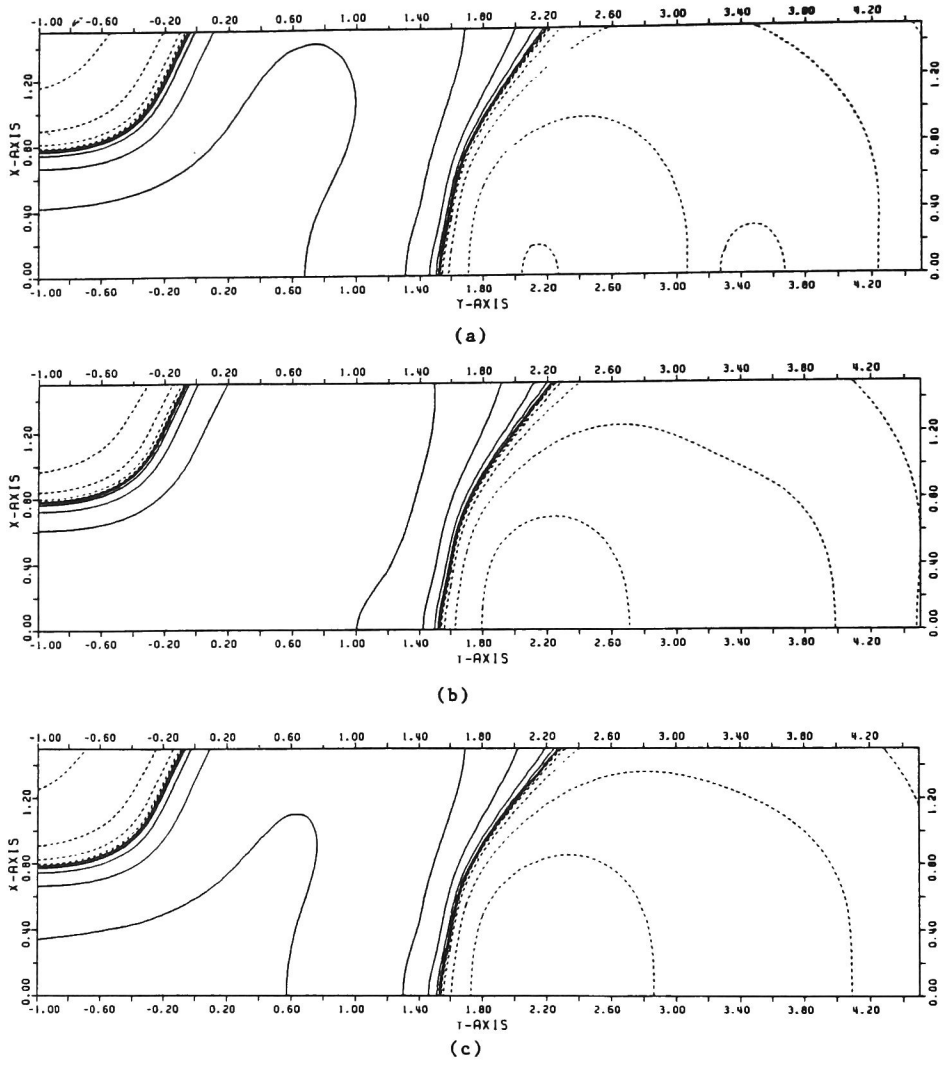

Fig. 6. Dynamic total electron transfer induced by mode ν_1. The meaning of the figure the same as in Fig. 4. The values of the contours are also the same as in Fig. 4.

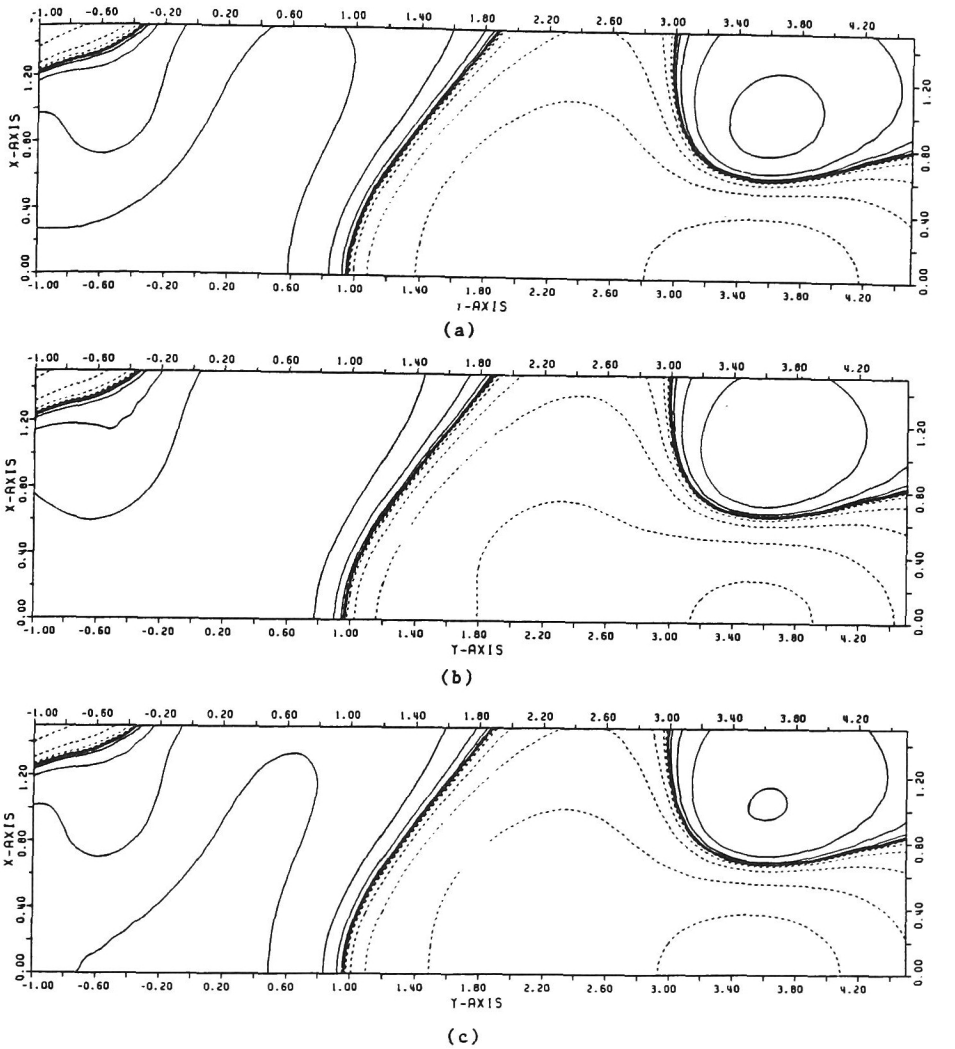

Fig. 7. Dynamic σ-electron transfer induced by mode ν_2. The meaning of the figure is the same as in Fig. 4. The values of the contours are $\pm 1.0 \times 10^{-n}$ (n = 3, 4, 5, 6), $\pm 3.0 \times 10^{-n}$ (n = 4, 5, 6), and 0.0; 1.0×10^{-3} is omitted in (a) and (b), and -3.0×10^{-3} is added in (b) and (c).

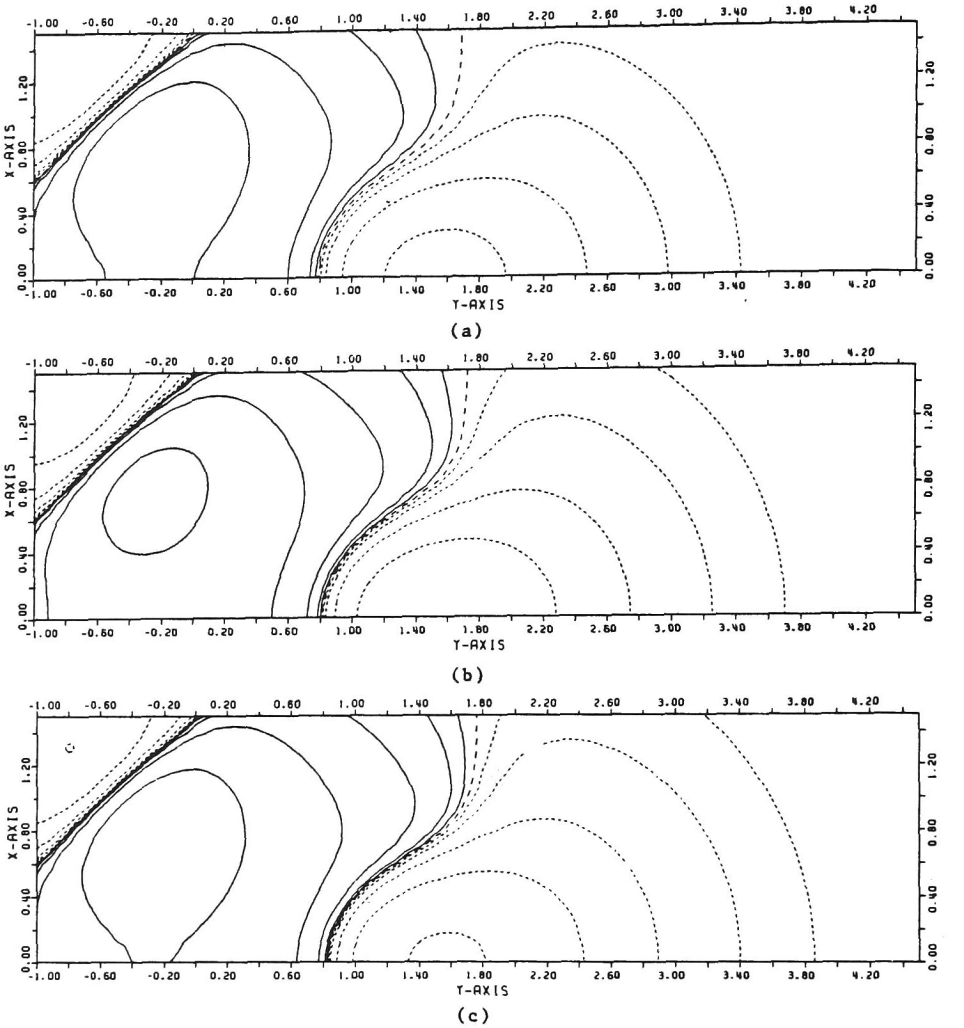

Fig. 8. Dynamic π-electron transfer induced by mode ν_2. The meaning of the figure is the same as in Fig. 4. The values of the contours are $\pm 1.0 \times 10^{-n}$ (n = 4, 5, 6), $\pm 3.0 \times 10^{-n}$ (n = 5, 6), and 0.0; $\pm 1.0 \times 10^{-4}$ are omitted in (a), and -3.0×10^{-4} is added in (c).

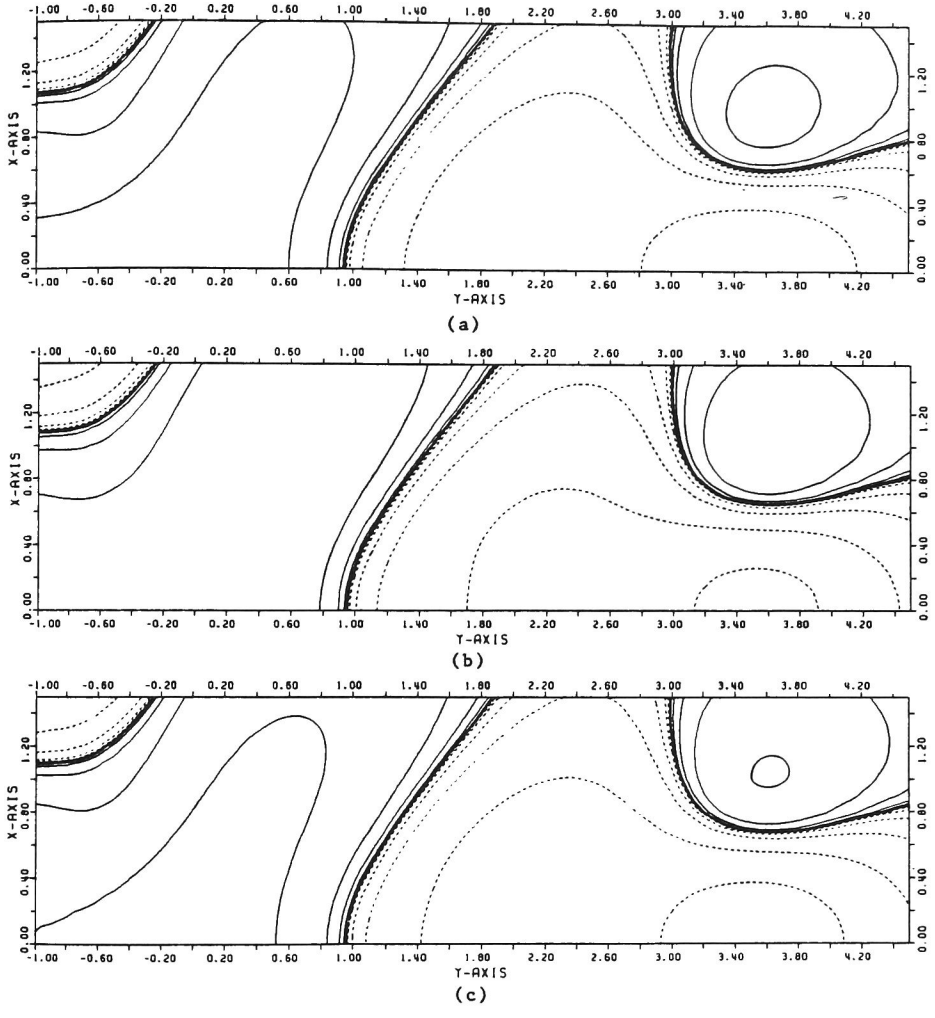

Fig. 9. Dynamic total electron transfer induced by mode ν_2. The meaning of the figure is the same as in Fig. 4. The values of the contours are the same as in Fig. 7.

vibrational modes. In the case of mode ν_1, the σ-electron on C_2 and C_3 is transferred away, while the σ-electron on C_1 grows significantly. On the other hand, in the case of mode ν_2, the σ-electron on C_1 is tranferred away, while the σ-electron on C_2 and C_3 grows slightly. These features are in contrast with those observed in the plane: the dynamic σ-electron current in the plane shows the monotonic decrease of electron density on carbon nuclei and symmetric electron transfer to both sides of carbon nuclei along the vector of the normal vibrational modes[23(a)]. The dynamic π-electron current shows that the π-electron density accumulates also inside of the ring. In the case of mode ν_1, a pair of lumps are formed on the C_2-C_3 bond region, and a large lumps is formed in the neighborhood of C_1. On the other hand, in the case of mode ν_2, a pair of lumps are formed along the C_1-C_2 bond and along the C_1-C_3 bond. The centers of the lumps of the dynamic π-electron current differ those of the σ-electron current. It should be noted that all the π-electrons are flowing from the carbon center to the cation center which is formed in the course of the normal vibrations. Consequently, the accumulations of the π-electron density occurs inside of the ring.

Thus, the characteristics of the dynamic σ- and π-electron currents have been obtained. This may yield an interesting dynamic effect on the σ-electron participation in

the ring current model of aromatic compounds or the electron conductivity of conjugated systems.

B. Radical Abstraction Reaction.

The potential profile along the IRC of the reaction CH_3 + H_2 -> CH_4 + H is shown in Fig.10. This reaction is calculated to be exothermic reaction by 3.9 kcal/mol, and to have the barrier height of 20.6 kcal/mol. The transition state is located at the origin and the IRC is negative at the reactant side, and positive at the product side. The dynamic electron transfer accompanying the process of the reaction is given by Eq.(4).

Figs.11(a),11(b),and 11(c) show the dynamic spin transfer which accompanies the displacement vector of IRC of the reaction CH_3 + H_2 --> CH_4 + H , at the successive point s=-2.6, s=0.0, and s=3.6, respectively. As the reaction proceeds the domain where the dynamic spin transfer has the positive value grows inside of the reaction system. The nodal point changes accordingly and demonstrates the active electronic process along the reaction coordinate[49]. Thus, the dynamic spin transfer at each point on the reaction coordinates correlates with each other to create the the dynamic spin current in the course of the chemical reaction.

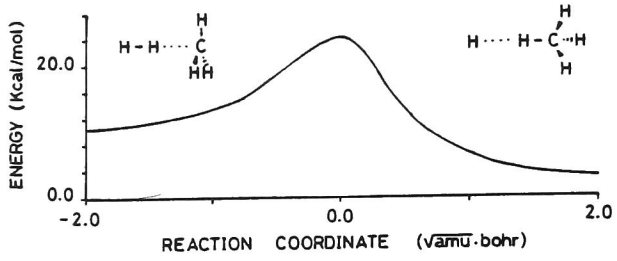

Fig. 10. Potential profile along the IRC. The transition state is located at the origin and the IRC is negative on the reactant side and positive on the product side.

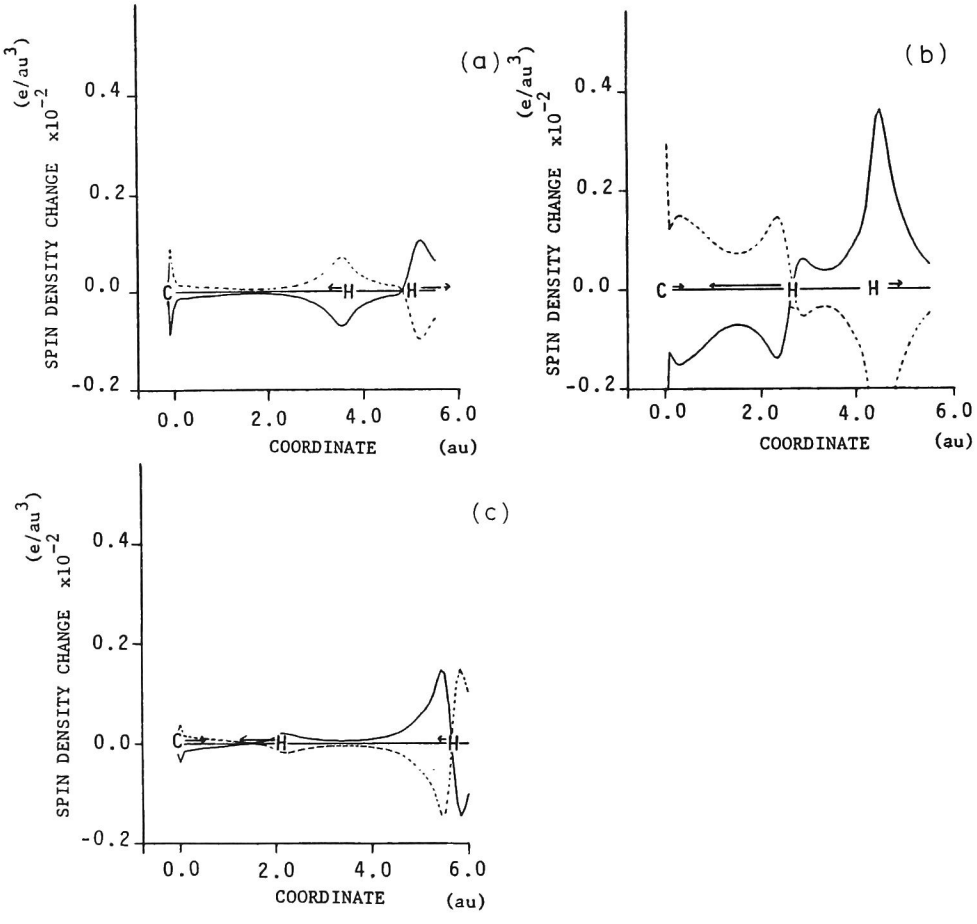

Fig. 11. Dynamic spin transfer accompanying the displacement vector of the IRC at successive points on the IRC: (a) $s = -2.5$, (b) $s = 0.0$, and (c) $s = 2.5$. The ω is chosen as follows: (a) 4647.1 cm^{-1} of the H_2 stretching mode, (b) 2215.3 cm^{-1} of the imaginary mode at the transition state, and (c) 3266.8 cm^{-1} of the C—H stretching mode of CH_4. Q_0 is chosen to be 0.5. The solid curve corresponds to the dynamic spin transfer from $t = -\tau/4$ to $t = 0$. The broken curve corresponds to the dynamic spin transfer in the backward direction from $t = -\tau/4$ to $t = -\tau/2$. The spin density is calculated on the molecular axis along which the reaction proceeds. The location of the atoms and the displacement vector are depicted in the figure.

Figs.12(a) and 12(b) show the dynamic spin transfer accompanying the vibrational modes 1 and 2, which are orthogonal to IRC at the transition state. The vibrational mode 1 has a large component of 0.7 of the out-of-plane mode of CH_3 . Since the out-of-plane mode of CH_3 does not have a large component in the IRC displacement vector from the component analysis of IRC, the mode 1 can be characterized as the bath mode which does not intervene in the reaction process. Comparing Fig.12(a) with Fig.11(b), the dynamic spin transfer which accompanies the bath mode does not closely correlates with the dynamic spin transfer accompanying the reaction process. On the other hand, the vibrational mode 2 has a large component 0.6 of the stretching mode of H_2. Since the stretching mode of H_2 has a large component in the IRC displacement vector, the mode 2 is characterized as the system mode which couples strongly with the reaction process. Comparing Fig.12(b) with Fig.11(b), the dynamic spin transfer which accompanies the system mode correlates quite well with the dynamic spin transfer accompanying the reaction process. Thus it can be concluded that the system mode enhances the dynamic spin current accompanying the reaction process, and the bath mode perturbs it. Also, comparing Fig.12(b) with Fig.11(a), it should be noted that the feature of the dynamic spin transfer which accompanies the mode 2 at the saddle point is similar to that of the dynamic spin transfer accompanying

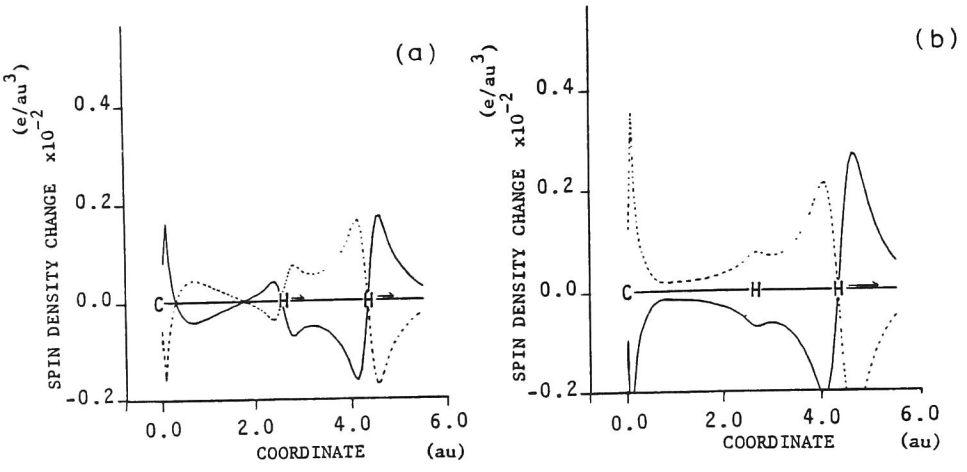

Fig. 12. Dynamic spin transfer accompanying the vibrational modes orthogonal to the IRC at the transition state: (a) the mode 1 with ω = 1250.7 cm^{-1}, and (b) the mode 2 with ω = 1507.8 cm^{-1}. The meaning of the figure is the same as in Fig. 11.

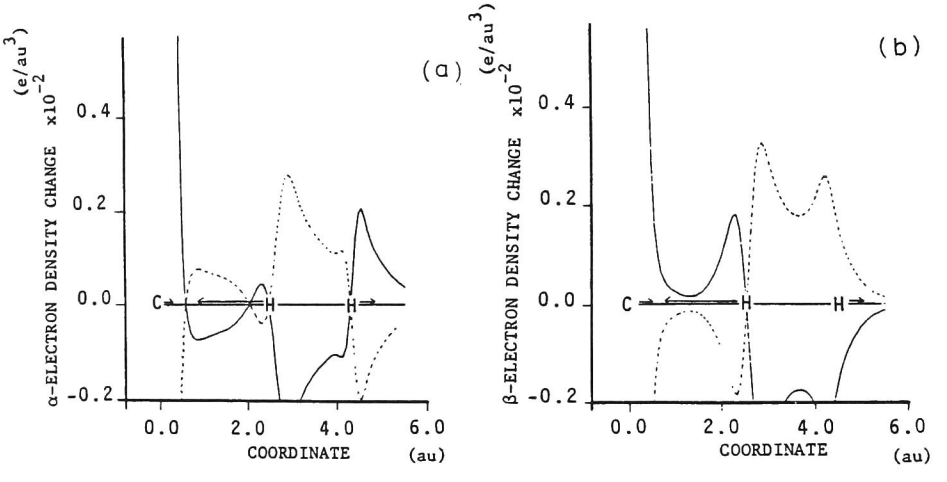

Fig. 13. (a) Dynamic α-electron transfer, and (b) dynamic β-electron transfer at the transition state. The meaning of the figure is the same as in Fig. 11(b).

the reaction process at the early stage of the reaction. This is because the mode 2 has the component of the relative translational motion of H_2 molecule.

Figs.13(a) and 13(b) show the dynamic electron transfer of α-spin electron and β-spin electron, accompanying the displacement vector of IRC at the transition state, respectively. In the H-H bond region, both figures show the negative electron transfer in the course of the reaction. This clearly represents the scission of the H-H bond. The accumulation of the β-spin electron in the C-H bond region is remarkable and contributes to the formation of the new bond. Interestingly, comparing Fig.13(a) with Fig.12(a), the similarity of the dynamic α-electron transfer accompanying the reaction process at the saddle point with the dynamic spin transfer accompanying the bath mode at the saddle point is found. It follows that the bath mode is clearly correlated with the dynamic α-electron current of the reaction process at the saddle point.

Now, we shall examine the isotope effect of the dynamic spin transfer accompanying the reaction process at the transition state, which cannot be analyzed by the static method. This is shown in Fig.14. Comparing Fig.14 with Fig.11(b), it is found that, as the projectile H_2 molecule is isotopically substituted by D_2, the dynamic spin transfer is suppressed everywhere. This shows that the isotopic

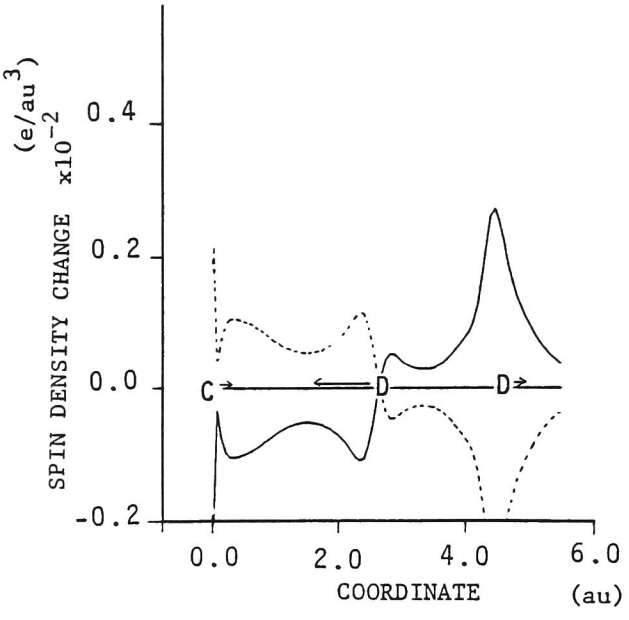

Fig. 14. Isotope effect of the dynamic spin transfer corresponding to Fig. 11(b): the ω is 1629.1 cm^{-1}, and the meaning of the figure is the same as in Fig. 11(b).

substitution suppresses the cleavage of the old bond and the formation of the new bond. It follows that the regular isotope effect observed in this reaction[46] correlates well with this dynamic analysis of the electronic structure. Thus, the study of the dynamic electron current induced by molecular vibration may provide us with a new aspect of the chemical reaction dynamics.

IV. CONCLUDING REMARKS

In the present chapter, the dynamic electron current induced by molecular vibration has been studied. In cyclopropenyl cation, the characteristic distributions of the dynamic σ- and π- electron currents have been revealed and the relation with the ring current model has been discussed. The properties of the dynamic electron current may play an important role also for the design of molecular device. In the radical abstraction reaction $CH_3 + H_2 \rightarrow CH_4 + H$ the dynamic spin currents associated with the nuclear motion along the reaction coordinate has been examined. The dynamic spin currents induced by the vibrational motion perpendicular to the reaction coordinate show the characteristic modes of correlation with the dynamic spin current along the reaction coordinate. The dynamic electron transfer may provide us with

the new aspects of the reaction process, in particular, from the viewpoint of the quantum fluid dynamics[50]. Finally, it should be noted that we have shown the stationary and mean electron densities and their differences induced by the dynamical motion of nuclei. Further feedback of energy from the electrons to nuclei will be important for the study of the vibronic stability of molecular systems. In order to treat more subtle problems, such as electron transfer reaction in biological systems or inner sphere electron transfer reaction in the transition metal complex, more sophisticated wavefunction should be used, and then the novel correlation of the dynamic electron current with the dynamics of molecular vibration may be revealed.

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Chapter 3

The Analysis of the Coherent Property of the Electron Current and the Intermolecular Interaction Induced by the Molecular Vibration in the Course of the Chemical Reaction

I. INTRODUCTION

The energy transfer process which is the reverse side of the electron transfer process is important for the microscopic chemical reaction process. The important role of the energy transfer process among the molecular vibrations in the chemical reaction dynamics has been discussed actively both theoretically[1,2] and experimentally[3,4]. The two processes of energy transfer and electron transfer are the two sides of a single relaxation process. This is because the rearrangement of atoms which is brought about by the energy transfer process causes the electron transfer in the molecule. Moreover the redistribution of electrons makes a strain in the molecule to modify the nuclear dynamics. In the discussion mentioned above, the terminology of "the electron transfer" means the redistribution of electrons and does not always include the nonadiabatic transition process, though it usually involves the nonadiabatic transition process tacitly in the theoretical study of the inorganic and biological systems[5,6]. The usual meaning of the word is one of the special case of that used

here. In most chemical reactions where the nonadiabatic couplings can be neglected, the electron transfer process is still important because it represents the total dynamics of the molecule.

In the study of chapter 2 of this part, the dynamic electron current accompanying a chemical reaction was studied and some dynamic aspects such as the vibrational mode specificities and the isotopic effects of the chemical reaction were investigated. The dynamic electron current which accompanies a motion of a wavepacket along the Intrinsic Reaction Coordinate (IRC) converges to satisfy the rigid additive property at a stable equilibrium point of the potential energy surface. Though the mode specific character of the dynamic electron current was already investigated in chapter 2, the vibrationally induced electron transfer process accompanying the energy transfer process remains still an interesting problem to be investigated theoretically. Here the methodology of the reaction ergodography[7,8] is useful. The IRC which is a general extension of the normal coordinate of the molecular vibration to the large amplitude motion of nuclei[9] can be said from its definition[10] to be also the path of the nuclear motion on the potential energy surface with the infinitesimal velocity. Thus the displacement vector of the IRC corresponds to the directional vector of the intrinsic motion of the nuclei with the infinitesimal velocity. If the

displacement vector is expanded using the complete and orthonormal fixed vectors and the expansion coefficients are traced along the IRC, the energy transfer process of the intrinsic motion of nuclei with the infinitesimal velocity is represented through the change of the expansion coefficients. This characterizes to the intrinsic energy transfer process. If the directional vectors of the translational and rotational motion and the normal vibrational vectors of the composite fragments in their stable equilibrium structure are used to construct the orthonormal and complete basis vectors of chemical reacting system, the analysis of the intrinsic energy transfer process makes it clear how the nuclear motions of the composite fragments contribute the intrinsic motion of the total chemical reacting system. The stable limit theorem which[9] shows that the IRC converges most probably to the weakest normal vibrational mode at the stable equilibrium point of the potential surface prefers a single kind of participation of the nuclear motions of the composite fragments. In the collisional chemical reaction, the IRC converges to the translational motion which leads to a collision of the two composite fragments, though at the bottleneck region of the potential energy surface the various nuclear motions participate in the displacement vector of the IRC. This characterizes the coherent property of the intrinsic energy transfer process. It is interesting to discuss how this

coherent property of the intrinsic energy transfer process affects the vibrationally induced electron current. The coherent property of the dynamic electron current is studied by expanding it on the same footing as the expansion of the displacement vector of the IRC. Here, the local tangent approximation in the curved space of 3N dimensional space of nuclei is used to transform the coordinate variables, and the quantum effect of the molecular vibration on the electron density is estimated in the local tangent plane. By tracing the dynamic electron current along the IRC,[11] the coherent property of the intrinsic electron transfer which also reflects the quantum effect of the molecular vibration can be investigated. In this chapter, the coherent property of the intrinsic spin transfer process of the following radical reaction;

$$CH_3+CH_4 \rightarrow CH_4+CH_3, \qquad (I)$$

is studied. The dynamic spin transfer of the reaction (I) itself is studied in part of chapter 3 of part III. The vibrationally induced intermolecular interaction and its coherent property is also studied for this reaction. This is achieved by estimating the dipole fluctuation of the two composite fragments of the chemical reacting system within the supermolecule model and by calculating how the quantum effect of molecular vibration acts to induce the intermolecular interaction or not. Then the coherent property is also

analyzed and traced along the IRC. These studies enable us to study the dynamic electron current accompanying the energy transfer process.

II. THE EXPANSION OF THE DYNAMIC ELECTRON CURRENT

The dynamic electron density $\langle \rho \rangle$ or the dynamic dipole moment $\langle \vec{\mu} \rangle$ which reflects the quantum effect of a molecular vibration is defined as follows;[11-13]

$$\langle P \rangle = \int P \Psi_{nuc}^{*} \Psi_{nuc} dQ \ , \tag{1.a}$$

$$P=\rho \ or \ P=\vec{\mu} \ , \tag{1.b}$$

where ρ and $\vec{\mu}$ are the electron density and the electric dipole moment in the clamped nuclei limit. The nuclear wavefunction and the normal coordinate for the molecular vibration are denoted by Ψ_{nuc} and Q, respectively. If the harmonic approximation is adopted for P with respect to Q, and if the harmonic oscillator wavefunction is substituted in Ψ_{nuc} , then the dynamic electron density $\langle \rho \rangle$ or the dynamic dipole moment $\langle \vec{\mu} \rangle$ satisfies the following additive property[11-13] which shows that it is linear with respect to the quantum number ν of the molecular vibration;

$$\langle P \rangle_{nuc} \sim P(0) + (1/2\omega)(\partial^2 P/\partial Q^2)(0)(\nu + 1/2), \tag{2}$$

where ω is the frequency of the molecular vibration. If the oscillating wavepacket wavefunction $\Psi_{wavepacket}$;

$$\Psi_{wavepacket} = (\omega/\pi)^{1/4} \exp\left[-(1/2)\omega(Q - Q_0 \cos\omega t)^2 \right.$$

$$-i\{(1/2)\omega t+\omega QQ_0\sin\omega t-(1/4)\omega Q_0^2\sin 2\omega t\}] \quad , \tag{3}$$

is substituted in Ψ_{nuc} , the time dependent dynamic electron density[11-13] or the time dependent dynamic dipole moment is given as follows;

$$\langle P\rangle_{wavepacket}\sim P(0)+(\partial P/\partial Q)(0)Q_0\cos\omega t$$
$$+(1/2)\ (\partial^2 P/\partial Q^2)(0)\{1/(2\omega)+(Q_0\cos\omega t)^2\}, \tag{4}$$

where the Q_0 and t denote the initial displacement of the wavepacket and the time parameter, respectively. The dynamic electron density[11] (dynamic dipole moment) and time dependent dynamic electron density (time dependent dynamic dipole moment) of the polyatomic molecule which has some vibrational modes are easily derived to give the following expression;

$$\langle P\rangle_{n_1,n_2,\ldots,n_{natoms}}\sim\ P(0)$$
$$+\sum_j(1/2\omega_j)(\partial^2 P/\partial Q^2)(0)(\nu_j+1/2), \tag{5.1}$$

$$\langle P\rangle_{wavepacket}\ \sim\ P(0)+\sum_j(\partial P/\partial Q_j)(0)Q_{0j}\cos\omega_j t$$
$$+(1/2)\sum_j(\partial^2 P/\partial Q_j{}^2)(0)\ \{1/2\omega_j+(Q_{0j}\cos\omega_j t)^2\}$$
$$+(1/2)\sum_{ij}(\partial^2 P/\partial Q_i\partial Q_j)(0)Q_{0i}Q_{0j}\cos\omega_i t\cos\omega_j t, \tag{5.2}$$

where ν_j,ω_j,Q_j, and Q_{0j} are the quantum number, the frequency, the normal vibrational coordinate, and the initial

displacement of the wavepacket of the j-th vibrational mode. And natoms denotes the total number of atoms contained in a molecule. The term $\partial^2 P/\partial Q_i \partial Q_j$ (0) which is included in $\langle P \rangle_{wavepacket}$ is important for the electron transfer process or the dipole fluctuation process accompanying the vibrational energy transfer between the two vibrational modes. The electron current accompanying the vibrational energy transfer will be more important where the nonadiabatic couplings are small. This is because the trajectory of the wavepacket[1,14,15] which travels among the distinct vibrational modes brings in the dynamic electron current induced by it.

Taking this situation into account, the dynamic electron current which is induced by the quantum effect of the nuclear motion along the IRC is expanded in the same way with the expansion of the displacement vector of the IRC $\vec{\xi}$ in the basis vectors $\vec{\upsilon}$ which is the direct product of the directional vectors of the translational motions, the rotational motions, and the normal vibrational motions of the two composite fragments A and B; $\{\vec{\upsilon}_A\}$ and $\{\vec{\upsilon}_B\}$, respectively;

$$\vec{\xi} = \sum_n c_n \vec{\upsilon}_n , \tag{6.1}$$

$$\{\vec{\upsilon}_n\} = \{\vec{\upsilon}_A\} \otimes \{\vec{\upsilon}_B\} \tag{6.2}$$

where $\{c_n\}$ is a set of expansion coefficients. As mentioned before, the stable limit theorem[9] prefers a single kind of participation of the nuclear motions at the stable point.

Therefore a set of expansion coefficients $\{c_n\}$ will be such that only one expansion coefficient is 1 and the other expansion coefficients are all zero at the stable point. The reaction is not collisional in this case and the set of expansion coefficients for the collisional reaction $\{c_n\}$ will be such that only the two expansion coefficients of the translational motions leading to a collision between the two fragments will have nonzero values at the stable point. On the other hand, all the expansion coefficients have non zero values in the non stable regions of the potential energy surface such as the transition state. This characterizes the coherent property of the intrinsic energy transfer process. The second derivative of the spin density which is related to the dynamic electron current induced by the quantum effect of the nuclear motion along the IRC; $\partial^2\rho(0;s)/\partial s^2$ in which the center of the wavepacket is at s of the IRC can be expanded as follows;

$$(\partial^2/\partial s^2)\rho(0;s)=\sum_n c_n{}^2(\partial^2/\partial Q_n{}^2)\rho(0;s)$$

$$+\sum_{mn} c_n c_m(\partial^2/\partial Q_m\partial Q_n)\rho(0;s), \qquad (7)$$

where $\{Q_n\}$ are the global coordinate whose directional vectors are $\{\vec{u}_n\}$. The local tangent approximation is used to transform the derivatives of the coordinate variables in Eq.(7). The quantum effect of the molecular vibration on the

electronic structure of the molecule is also estimated in that approximation. The second term of the right hand side of Eq.(7) is related to the dynamic electron current which is brought in by the cooperation of the two vibrational modes. By tracing the expansion given by Eq.(7), the coherent property of the intrinsic electron current induced by the quantum effect of the nuclear motion along the IRC can be investigated with the help of the full use of the IRC concept[10].

The vibrationally induced intermolecular interaction between the two fragments A and B is investigated through the analysis of $\langle \Delta\vec{\mu} \rangle$ where $\Delta\vec{\mu}$ is the dipole fluctuation between the two fragments in the clamped nuclei limit on the basis of the supermolecule model defined as follows;

$$\vec{\mu}_{total}=\vec{\mu}_A+\vec{\mu}_B+\Delta\vec{\mu}, \tag{8}$$

where $\vec{\mu}_{total}$ is the total dipole moment of the chemical reacting system. The same expansion of $(\partial^2/\partial s^2)\langle \Delta\vec{\mu} \rangle$ as in Eq.(7) is analyzed to investigate the coherent property of the vibrationally induced dipole fluctuation between the two composite fragments of the chemical reacting system.

III. THE INTRINSIC ENERGY TRANSFER PROCESS ALONG THE IRC

It is well known that the radical reaction in general is scarcely affected by its environment. For it the inter- and intra-molecular dynamics of the system is more important than

the other reactions. So it will be interesting to investigate the dynamics of the radical reaction theoretically, though the experimental study of the dynamics of the radical reaction may be difficult. The intrinsic dynamics of the radical reaction (I)[16] is studied. The coherent property of the dynamic electron current and the vibrationally induced dipole fluctuation are studied for this reaction.

The potential profile and the changes of the geometrical parameters along the IRC of the reaction (I) are depicted in Fig.1 and tabulated in Table 1, respectively. The transition state is located at the origin of the IRC; s=0.0, and the reactant (product) is located at the negative (positive) side of the IRC. The barrier height of the reaction is calculated to be 29.4 kcal/mol within the UHF scheme of Pople and Nesbet[17] by using the 4-31G basis set[18]. All the calculations in this chapter are performed within the same level of the calculation, if there is no special comment. The Gaussian80[19] and Gaussian82[20] programs with the requisite new additional subroutines are used in this study. This reaction can be said to be a characteristic proton transfer reaction because the distance between the terminal carbon atoms is kept almost constant during the atom transfer of the central proton. The large rise of the potential energy near the transition state may be mainly due to this bond alternation process.

The characteristic change of the expansion coefficients

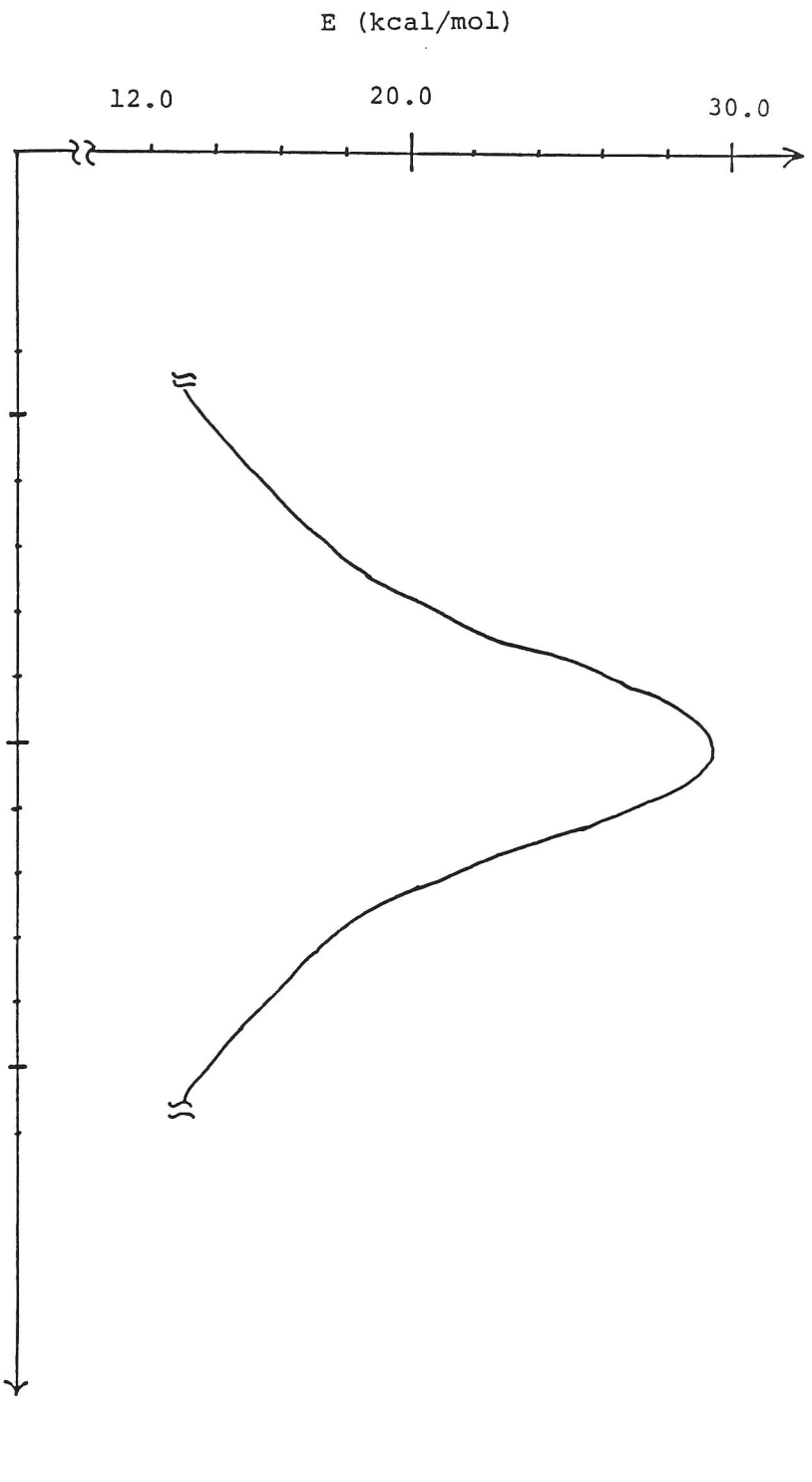
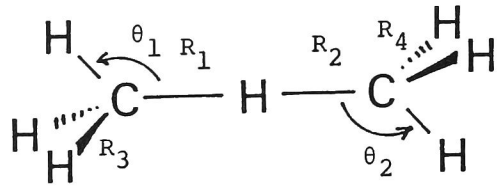


Fig. 1 The potential energy(E) profile along the IRC

Table 1 The change of the geometrical parameter along the IRC



s[a]	R_1^b	R_2^b	$R_1+R_2^b$	θ_1^c	θ_2^c	R_3^b	R_4^b
-1.0	1.0632	1.7362	2.7994	108.9	97.7	1.0816	1.0720
-0.9	1.0637	1.7165	2.7801	108.7	98.6	1.0815	1.0724
-0.8	1.0646	1.6970	2.7616	108.5	99.6	1.0814	1.0729
-0.7	1.0659	1.6781	2.7440	108.2	100.7	1.0812	1.0735
-0.6	1.0700	1.6581	2.7281	107.7	101.8	1.0812	1.0741
-0.5	1.1007	1.6174	2.7181	107.1	102.8	1.0811	1.0748
-0.4	1.1477	1.5662	2.7140	106.6	103.5	1.0806	1.0753
-0.3	1.1984	1.5138	2.7122	106.2	104.0	1.0800	1.0759
-0.2	1.2504	1.4610	2.7114	105.8	104.4	1.0792	1.0765
-0.1	1.3028	1.4082	2.7110	105.5	104.8	1.0784	1.0770
0.0	1.3555	1.3555	2.7110	105.1	105.1	1.0779	1.0779

[a]The letter s denotes the IRC of the reaction. The transition state is located at the origin and the IRC is negative(positive) on the reactant(product) side.... The unit of the IRC is $\sqrt{\text{amu}}\cdot\text{bohr}$.

[b]The bond lengths are denoted in angstrom units.

[c]The bond angles are denoted in degrees.

$\{c_n\}$ along the IRC are traced and shown in Fig.2. Some basis vectors $\{\vec{v}_n\}$ of Eq.(6.1) are drawn in the same figure. At the asymptotic region of the reactant side, the absolute values of the coefficients of the translational motions of CH_3 and CH_4 fragments are large. The coefficient of the out of plane vibrational motion of CH_3 fragment is extremal near the point s=-0.6, though its absolute value gets smaller at both the asymptotic region and the region near to the transition state. At the region near to the transition state, especially from s=-0.5 to s=0.0, the coefficient of the C-H stretching vibrational motion which contains mainly the motion of the transferred proton atom and the coefficient of the totally symmetric vibrational motion are large. Then, it can be said that the energy transfer from the translational motions which lead to the collision of the two composite fragments to the C-H stretching vibrational motion and the totally symmetric vibrational motion is important for the reaction. The out of plane vibrational motion of the CH_3 fragment also intervene in the energy transfer process. Ideally, the energy conversion from the collisional motion to the C-H stretching vibrational motion is the most important.

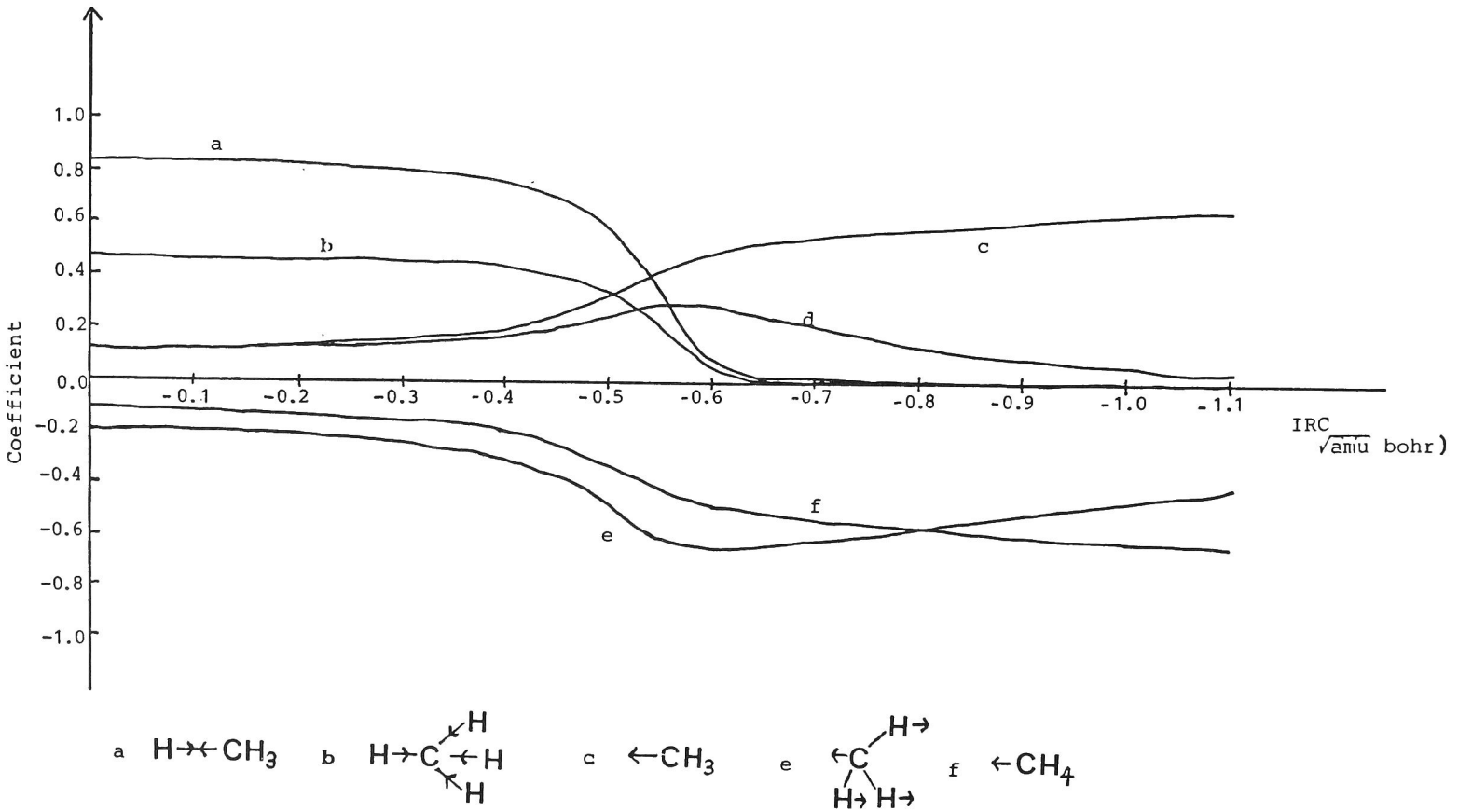


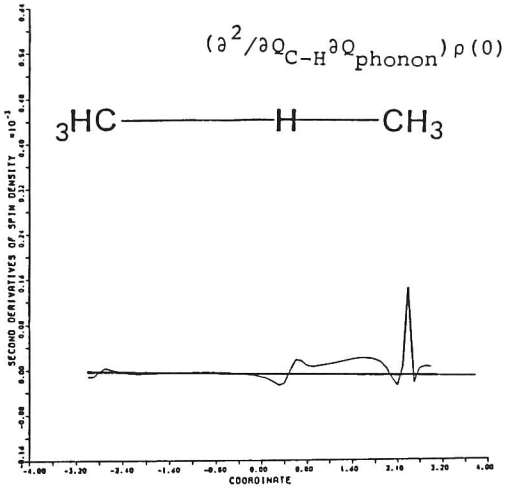
Fig.2 The change of the expansion coefficient along the IRC

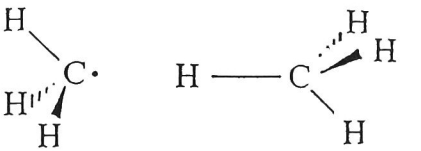
IV. THE COHERENT PROPERTY OF THE SPIN CURRENT INDUCED BY THE MOLECULAR VIBRATION ALONG THE IRC

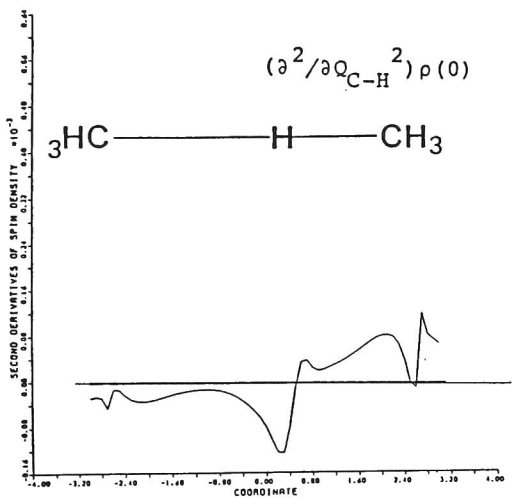
From the results obtained in section III of this chapter, it has been concluded that the intrinsic energy transfer process from the translational motions which lead to a collision between the two fragments, CH_3 and CH_4, to the C-H stretching vibrational motion of the CH_4 fragment is most important for the reaction (I). Then the coherent property of the electron current induced by this intrinsic energy transfer process will be important for the dynamic aspect of the electronic process of the reaction. The individual terms of the expansion of the second derivatives of the spin density ρ given by the right hand side of Eq.(7) are calculated and traced along the IRC of the reaction (I) for the translational motions and the C-H stretching vibrational motions. Figs. 3, 4, and 5 show the spatial distribution of the second derivatives of the spin density; $\partial^2/\partial Q_{CH}\partial Q_{trans}\ \rho\ (0;s)$, $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$ and $\partial^2/\partial Q_{trans}{}^2\rho(0;s)$ for s=-1.0, -0.5, and 0.0, respectively. Here, Q_{CH} and Q_{trans} are the global extension of the normal coordinates whose directional vectors are the C-H vibrational mode vectors and the vectors of the translational motions which lead to a collision between the two fragments, respectively. A positive value of the spin density means that the α-electron density is larger than that of β-electron and a negative value means that the β-electron

density is larger than that of α-electron. It can be seen from Fig. 3 that the three second derivatives of the spin density are positive in the carbon-proton bond which is to be cleaved, as the reaction proceeds, at s=-1.0, though the magnitudes are somewhat smaller compared with those of the three second derivatives at s=-0.5 and s=0.0, the magnitude of the spin density derivative in the carbon-proton bond is the largest for $\partial^2/\partial Q_{CH}^2\rho(0;s)$. The spatial distribution of all the three second derivatives of the spin density have peaks on the side of the terminal carbon atom of the CH_4 fragment. The second derivative of the spin density $\partial^2/\partial Q_{CH}^2\rho(0;s)$ is negative from the region; -2.8 bohr to 0.6 bohr and it is positive in the region; from 0.6 bohr to 2.6 bohr of the electron coordinate. The second derivative of the spin density $\partial^2/\partial Q_{CH}\partial Q_{trans}\,\rho(0;s)$ is positive in the region; from 0.6 bohr to 2.2 bohr of the electron coordinate and there is only a small region around the coordinate at 0.4 bohr where the spin density is negative on the molecular axis. The spatial distribution of the second derivative of the spin density $\partial^2/\partial Q_{trans}^2\,\rho(0;s)$ localizes strongly on the terminal carbon atoms. The second derivative of the spin density with respect to the IRC s is approximately represented at s=-1.0 as follows;

$$(\partial^2/\partial s^2)\rho(0;s) \sim 1.471\times10^{-5}(\partial^2/\partial Q_{CH}^2)\rho(0;s) + 7.865\times10^{-1}(\partial^2/\partial Q_{trans}^2)\rho(0;s) + 6.803\times10^{-3}(\partial^2/\partial Q_{CH}\partial Q_{trans})\rho(0;s). \quad (9)$$







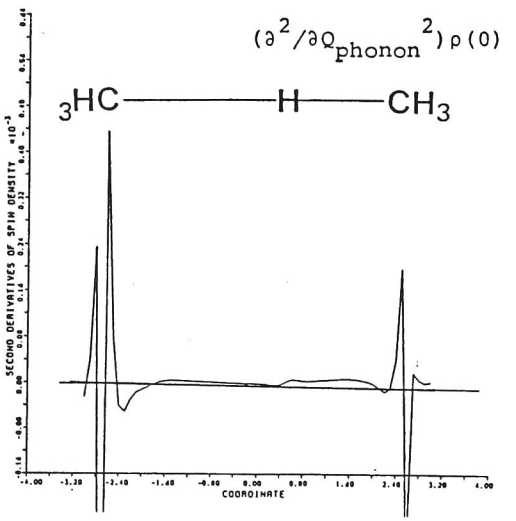
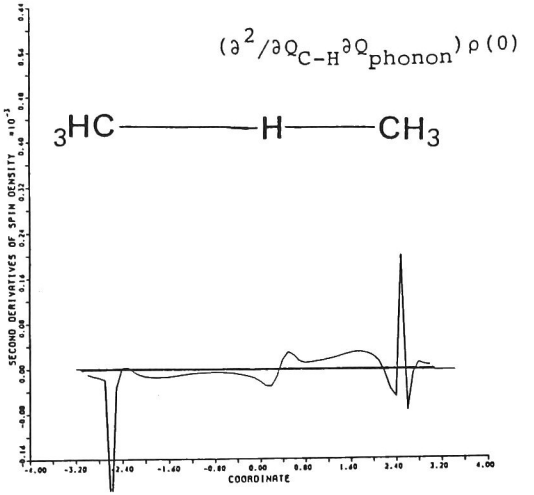
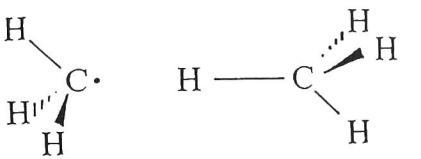
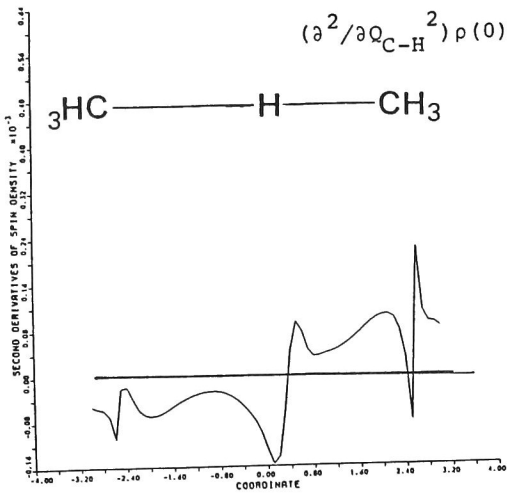


Fig.3 The second derivatives of the spin density with respect to the nuclear coordinates at s=-1.0 of the IRC

The dynamic spin current induced by the quantum effect of the molecular vibration along the IRC is $(1/4\omega)(\partial^2/\partial s^2)\rho(0;s)$. So the dynamic spin current is completely dominated by the second derivative $\partial^2/\partial Q_{trans}{}^2\ \rho(0;s)$, and therefore is small in the bonding region and localizes strongly on the terminal carbon atoms. Though the second derivatives $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$ and $\partial^2/\partial Q_{CH}\partial Q_{trans}\ \rho(0;s)$ are not small, they do not contribute so much to the intrinsic spin current induced by the quantum effect of the nuclear motion along the IRC. Fig.4 shows that all of these second derivatives of the spin density are positive in the carbon-proton bond which is to be cleaved as the reaction (I) proceeds at s=-0.5. The magnitudes are larger than those of s=-1.0, and less than those of s=0.0. The peaks of the spatial distributions of all the three second derivatives of the spin density tend to move from the side of the terminal carbon atom of the CH_4 fragment to the proton atom as the reaction proceeds from s=-1.0 to s=-0.5. The second derivative $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$ of the spin density is negative in the region from -3.0 bohr to 0.2 bohr and is positive from 0.4 to 2.4 of the electron coordinate. The spatial distribution of the second derivative of the spin density $\partial^2/\partial Q_{CH}\partial Q_{trans}\rho(0;s)$ at the bonding region is similar to that of $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$, though the magnitude is somewhat smaller. Again, the spatial distribution of the second derivative $\partial^2/\partial Q_{trans}{}^2\ \rho(0;s)$ of the spin density localizes







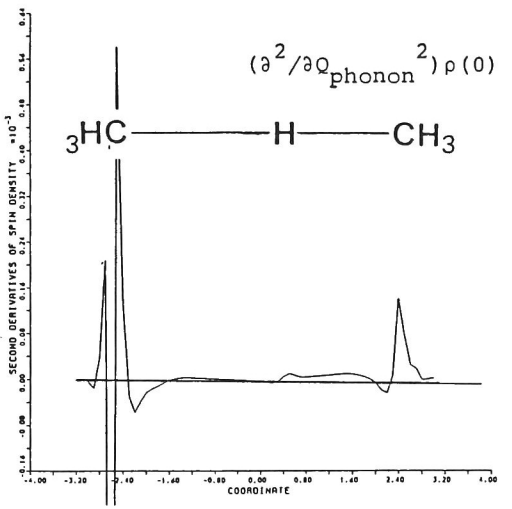


Fig.4 The second derivatives of the spin density with respect to the nuclear coordinates at s=-0.5 of the IRC

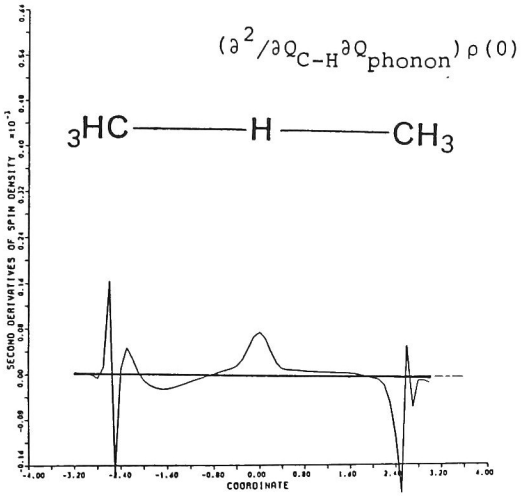
strongly on the terminal carbon atoms. The second derivative of the spin density with respect to the IRC s is approximately represented at s=-0.5 as follows;

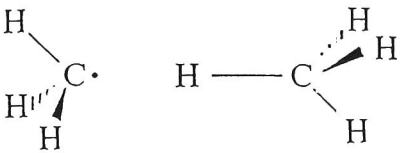
$$(\partial^2/\partial s^2)\rho(0;s) \sim 3.550\times10^{-1}(\partial^2/\partial Q_{CH}^2)\rho(0;s)$$
$$+2.200\times10^{-1}(\partial^2/\partial Q_{trans}^2)\rho(0;s)$$
$$+5.589\times10^{-1}(\partial^2/\partial Q_{CH}\partial Q_{trans})\rho(0;s). \quad (10)$$

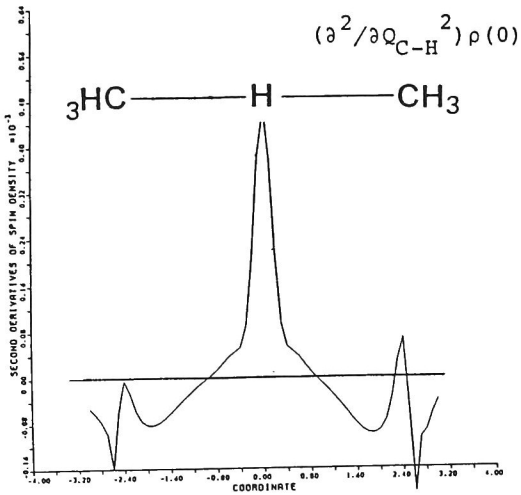
The most important contribution to the dynamic spin current induced by the quantum effect of the nuclear motions along the IRC is brought in by the second derivative $\partial^2/\partial Q_{CH}\partial Q_{trans}\ \rho(0;s)$, though the other second derivatives and $\partial^2/\partial Q_{CH}^2\rho(0;s)$and $\partial^2/\partial Q_{trans}^2\rho(0;s)$ contribute also to it significantly. The dynamic spin current accompanying the intrinsic energy transfer process from the translational motions, which lead to a collision between the two fragments, to the C-H stretching vibration plays an important role for the intrinsic spin current induced by the quantum effect of the nuclear motion along the IRC. Some assistance is brought in by the C-H stretching vibration and the translational motions.

Fig.5 shows that all the three second derivatives of the spin density have positive lumps around the transferred proton at the transition state s=0.0.

The peaks of the spatial distributions of all the three second derivatives of the spin density are located at the transferred proton. The magnitude of $\partial^2/\partial Q_{CH}^2\rho(0;s)$ is the largest among







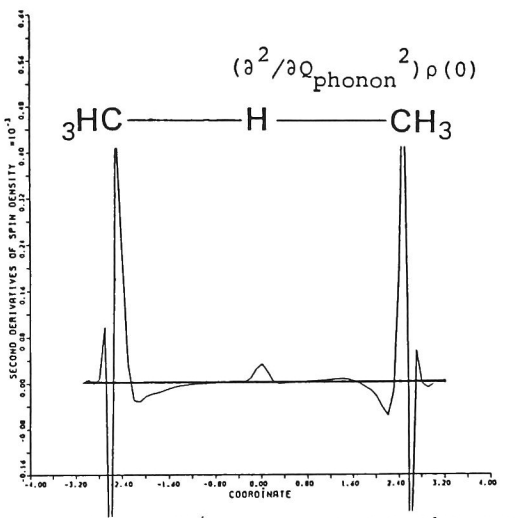


Fig.5 The second derivatives of the spin density with respect to the nuclear coordinates at s=0.0 of the IRC

the three second derivatives. The derivative $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$ has almost a symmetric distribution and is positive from -0.8 bohr to 0.8 of the electron coordinate and negative in the region from -3.0 to -0.8 and from 0.8 to 2.2 of the electron coordinate. The second derivative of the spin density $\partial^2/\partial Q_{CH}\partial Q_{trans}\,\rho(0;s)$ has an asymmetric distribution. It is negative from -2.0 to -0.8 and positive from -0.8 to 1.8 of the electron coordinate. The spatial distribution of the second derivative $\partial^2/\partial Q_{trans}{}^2\,\rho(0;s)$ localizes strongly on the terminal carbon atoms, though there is a small positive lump around the transferred proton. The second derivative of the spin density with respect to the IRC s is approximately represented at s=0.0 as follows;

$$(\partial^2/\partial s^2)\rho(0;s)\sim 6.986\times 10^{-1}(\partial^2/\partial Q_{CH}{}^2)\rho(0;s)$$
$$+2.886\times 10^{-2}(\partial^2/\partial Q_{trans}{}^2)\rho(0;s)$$
$$+2.840\times 10^{-1}(\partial^2/\partial Q_{CH}\partial Q_{trans})\rho(0;s). \qquad (11)$$

The most important contribution to the dynamic spin current induced by the quantum effect of the nuclear motion along the IRC is brought in by the second derivative $\partial^2/\partial Q_{CH}{}^2\rho(0;s)$ at s=0.0, though the contribution from $\partial^2/\partial Q_{CH}\partial Q_{trans}\,\rho(0;s)$ cannot be neglected. The dynamic spin current accompanying the C-H stretching vibration is most important for the dynamic spin current induced by the quantum effect of the nuclear motion along the IRC, though the dynamic spin current accompanying the intrinsic energy transfer process between the

translational motions which lead to a collision of the two fragments and the C-H stretching vibration also contributes to it.

The coherent property of the intrinsic spin current induced by the quantum effect of the nuclear motion along the IRC of the reaction (I) is clarified from these results. The initial intrinsic spin current is brought in by the dynamic spin current accompanying the translational motions which lead to a collision of the two fragments CH_3 and CH_4, and it is small because of the smallness of the dynamic spin current accompanying the translational motions. As the reaction proceeds, the dynamic spin current accompanying the intrinsic energy transfer process from the translational motions to the C-H stretching vibrational motions becomes important. At the transition state, the dynamic spin current accompanying the intrinsic energy transfer process has almost already completed and the current accompanying the C-H stretching vibrational motion become most important. These processes characterize the coherent property of the intrinsic spin current of the reaction (I).

V. THE COHERENT PROPERTY OF THE VIBRATIONALLY INDUCED INTERMOLECULAR INTERACTION ALONG THE IRC

It has been shown recently that the long-range

interaction potential between two molecules depends somewhat on the vibrational states of the molecules.[21] Then the long range molecular scattering potential is not same for the ground and excited states of the vibrational motion of the molecules. Therefore the coupling to the electric and magnetic fields or the effect of the photon field on the dynamics of the molecule cannot be neglected in the most rigorous study. The study of the nonlinear optical property of a molecule, which also takes into account the molecular vibration in the photon field, has begun recently, though a lucid theoretical study of the effect, which is applicable for all wavenumbers, based on the rigorous quantum mechanics is still expected. The new trends in the theoretical chemistry of this field will be continuously growing.

It is interesting to study how the molecular vibration acts to induce the intermolecular interaction in the chemical reacting system. The vibrationally induced dipole fluctuation between the two fragments CH_3 and CH_4 accompanying the chemical reaction (I) is studied to this end. The supermolecule model which is usual in the quantum chemical calculation is used to calculate the dipole fluctuation between the two fragments. The dipole fluctuation term $\Delta\vec{\mu}$ and the three second derivatives of the dipole interaction term $\partial^2/\partial Q_{CH}{}^2 \Delta\vec{\mu}$, $\partial^2/\partial Q_{trans}{}^2 \Delta\vec{\mu}$, and $\partial^2/\partial Q_{CH}\partial Q_{trans} \Delta\vec{\mu}$ are traced along the IRC of the reaction (I) and they are summarized in

Table 2. The dipole fluctuation and the second derivatives of the dipole fluctuation are zero for the direction orthogonal to the molecular axis. The dipole fluctuation along the molecular axis is negative (-0.136 debye) at the initial stage of the reaction (s=-1.0) and it becomes nearly zero (-0.0782 debye) as the reaction proceeds (s=-0.5) and then positive (0.2506 debye) at the transition state (s=0.0). The second derivative $\partial^2/\partial Q_{trans}{}^2 \Delta\mu_z$ is calculated to be always small in the course of the reaction. The second derivative $\partial^2/\partial Q_{CH}{}^2 \Delta\mu_z$ is calculated to be small at the initial stage of the reaction (s=-1.0) and it becomes positive (0.908 debye/au^2) as the reaction (s=-0.5) proceeds and then negative (-0.968 debye/au^2) (s=-1.0) at the transition state. The second derivative $\partial^2/\partial Q_{CH}\partial Q_{trans} \Delta\mu_z$ is calculated to behave similarly with the second derivative $\partial^2/\partial Q_{CH}{}^2 \Delta\mu_z$ during the reaction, though its magnitude is somewhat smaller. The second derivative of the dipole fluctuation $\Delta\vec{\mu}$ with respect to the IRC s is approximately represented at s=-1.0 as follows;

$$(\partial^2/\partial s^2)\,\Delta\vec{\mu} \sim 1.471\times10^{-5}(\partial^2/\partial Q_{CH}{}^2 \Delta\vec{\mu}) + 7.865\times10^{-1}(\partial^2/\partial Q_{trans}{}^2 \Delta\vec{\mu}) + 6.803\times10^{-3}(\partial^2/\partial Q_{CH}\partial Q_{trans} \Delta\vec{\mu}). \quad (12)$$

The vibrationally induced dipole fluctuation between the two fragments is $(1/4\omega)(\partial^2/\partial s^2 \Delta\vec{\mu})$. Thus the vibrationally induced dipole fluctuation is completely dominated by the

Table 2 The dipole fluctuation and its second derivatives with respect to the nuclear coordinates

s	$\Delta\mu_z$	$(\partial^2\Delta\mu_z/\partial Q_{CH}^2)$	$(\partial^2\Delta\mu_z/\partial Q_{trans}^2)$	$(\partial^2\Delta\mu_z/\partial Q_{CH}\partial Q_{trans})$
-1.0	-0.1360	-0.0565	0.0572	0.0633
-0.5	-0.0782	0.9080	0.0950	0.2170
0.0	0.2506	-0.9680	-0.0572	-0.1699

[a]The molecular axis lies on the z-axis.

The dipole fluctuation in debye units and the second derivatives of the dipole fluctuation in units of (debye/bohr^2) are zero for the direction orthogonal to the molecular axis.

The methane fragment is located on the positive side of the z-axis and the methyl radical fragment is located on the negative side.

[b]The letter s denotes the IRC of the reaction. The transition state is located at the origin and the IRC is negative(positive) on the reactant(product) side.

The unit of the IRC is $\sqrt{\text{amu}}\cdot$bohr.

second derivative $\partial^2/\partial Q_{trans}{}^2 \Delta\vec{\mu}$ and is small due to the smallness of the absolute value of this second derivative. On the other hand, the absolute value of the static dipole fluctuation is not small and the fluctuation is introduced by the electron flow between the CH_4 fragment and the CH_3 fragment. The static dipole interaction is more important than the vibrationally dipole interaction at the initial stage of the reaction (s=-1.0). At that point the vibrational state of the fragment does not greatly affect the initial stage of the reaction (I). The second derivative of the dipole fluctuation $\vec{\mu}$ with respect to the IRC s is approximately represented at s=-0.5 as follows;

$$(\partial^2/\partial s^2)\,\Delta\vec{\mu} \sim 3.550\times10^{-1}(\partial^2/\partial Q_{CH}{}^2\,\Delta\vec{\mu}) + 2.200\times10^{-1}(\partial^2/\partial Q_{trans}{}^2\,\Delta\vec{\mu}) + 5.589\times10^{-1}(\partial^2/\partial Q_{CH}\partial Q_{trans}\,\Delta\vec{\mu}). \quad (13)$$

All the three second derivatives contribute significantly to the vibrationally induced dipole fluctuation. The most important contribution is brought in by the second derivative $\partial^2/\partial Q_{CH}\partial Q_{trans}\,\Delta\vec{\mu}$, though the actual magnitude of the vibrationally induced fluctuation comes most from the second derivative $\partial^2/\partial Q_{CH}\,\Delta\vec{\mu}$ due to the largeness of its absolute value. The vibrationally induced dipole fluctuation between the two fragments is large, though the absolute value of the static dipole fluctuation is small. The vibrationally induced dipole fluctuation, which is mainly induced by the stretching

vibration and the intrinsic energy transfer process between the C-H stretching vibration and the translational motions which lead to a collision between the two fragments, is larger than the static dipole fluctuation. So the vibrationally induced dipole fluctuation is important at the halfway of the reaction process to keep the nonrigid intermolecular interaction between the two fragments. The vibrational state of the fragments affects ultimately on the halfway stage of the reaction process. The second derivative of the dipole interaction $\Delta\vec{\mu}$ with respect to the IRC s is approximately represented at s=0.0 as follows;

$$(\partial^2/\partial s^2)\Delta\vec{\mu} \sim 6.986\times10^{-1}(\partial^2/\partial Q_{CH}{}^2\Delta\vec{\mu}) + 2.286\times10^{-2}(\partial^2/\partial Q_{trans}{}^2\Delta\vec{\mu}) + 2.840\times10^{-1}(\partial^2/\partial Q_{CH}\partial Q_{trans}\Delta\vec{\mu}). \quad (14)$$

The contributions from the second derivatives $\partial^2/\partial Q_{CH}{}^2\Delta\vec{\mu}$ and $\partial^2/\partial Q_{CH}\partial Q_{trans}\Delta\vec{\mu}$ to the vibrationally induced dipole fluctuation are the main ones. The most important contribution is brought in by the second derivative $\partial^2/\partial Q_{CH}{}^2\Delta\vec{\mu}$. The vibrationally induced dipole fluctuation, which is induced mainly by the C-H stretching vibration and supported by the intrinsic energy transfer process between the C-H stretching vibration and the translational motions which lead to a collision between the two fragments is large at the transition state. In addition, the absolute value of the static dipole fluctuation is not small and the fluctuation is introduced by

the electron flow from the CH_3 fragment to the CH_4 fragment, which is the reverse direction to that of the vibrationally induced dipole fluctuation. At the transition state, both the static fluctuation and the vibrationally induced dipole fluctuation, which may decelerate the increase of the dipole fluctuation, are important. The vibrational state of the fragments affects partially the reaction process when the static fluctuation is also important. The vibrational excitation of the C-H stretching mode of the CH_4 fragment will diminish the total intermolecular interaction at the transition state.

It is clearly shown that the intermolecular interaction in the course of the reaction (I) depends on the vibrational states of the fragment molecules.

IV. CONCLUDING REMARKS

The dynamic electron current induced by the energy transfer process has been shown to be important for the dynamic aspect of the chemical reaction. The dynamic electron current studied here does not take into account the nonadiabatic transition process and hence represents an transport property of the electron accompanying the molecular vibration. The coherent property of the dynamic electron current in the course of the chemical reaction is clarified by

the full utilization of the IRC concept. The dynamic electron current initially induced by a single collective motion of nuclei is converted to another dynamic electron current accompanying the other vibrational motions and then finally it again converges to a single dynamic electron current induced by a single collective motion of the nuclei. The dipole fluctuation depends largely on the vibrational states of the fragments in the course of the chemical reaction (I). Especially, the vibrationally induced dipole fluctuation is important to include the nonrigid intermolecular interaction at s=-0.5, where the static dipole fluctuation is small. The importance of the vibrationally induced dipole fluctuation accompanying the energy transfer process is verified again.

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Chapter 4

Conclusion

In part II of this thesis, the dynamic electron current induced by the quantum effect of the molecular vibration in the course of the chemical reaction has been analyzed.

In chapter 2 of this part, the dynamic aspects of the chemical reaction such as the vibrational mode specificity and the isotopic effect were analyzed to discuss how these affect the dynamic electron current in the radical reaction; $CH_3 + H_2 \rightarrow CH_4 + H$. The analysis of the reaction ergodography of the reaction gives the system or bath classification of the vibrational mode. The system vibrational mode strongly couples with the IRC and intervenes in the chemical reaction process. The bath vibrational mode does not intervene in the chemical reaction process. The dynamic spin current induced by the motion of the wavepacket along the IRC was shown to have a smooth space distribution and to change as the reaction proceeds. On the other hand; the dynamic spin current induced by the bath mode vibration interrupts the smooth electron current accompanying the reaction process. The vibrational mode specificity in the energy transfer process brings in the strong mode specificity of the dynamic electron current. The isotopic substitution affects the total amount of the dynamic electron current. When the isotopic substitution from H_2 to D_2

is made, the dynamic electron current is suppressed everywhere. The dynamic electron current reflects the regular isotopic effect of the reaction well. The participations of the α- and β-electron current in the dynamic spin current were analyzed. It has been concluded that the bath mode is clearly correlated with the α-electron current. The dynamic electron current induced by the doubly degenerate molecular vibrations of the cyclopropenyl cation discussed in chapter 2 of part I in this thesis was analyzed in more detail. The participations of the σ-, and π-electron currents in the dynamic electron current were analyzed. The paramount σ-electron participation was demonstrated. The dynamic effect of the molecular vibration on the ring current of an aromatic compound whose diamagnetic current of σ-electrons has received much attention was discussed successfully.

In chapter 3 of this part, the coherent property of the dynamic electron current induced by the quantum effect of the molecular vibration in the course of the chemical reaction process has been discussed. The coherent property discussed here is such that the contributions from the various vibrational motions to the reaction process change so that a single kind of nuclear motion is dominant at the initial and final stage of the reaction process while the reaction process is shared by various nuclear motions during the reaction. It is interesting to remember the coherent property of the phase

factor of a wavefunction in the context of the fundamental problems of quantum mechanics. The coherent property in the chemical reaction process is entirely dependent on the IRC concept, especially the stable limit theorem. The coherent property of the intrinsic energy transfer process of the radical reaction; $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ was analyzed to investigate the coherent property of the intrinsic electron transfer process in the course of a chemical reaction process. The importance of the electron transfer process accompanying the energy transfer process in a chemical reaction is strongly emphasized. Also an important vibrational effect on the intermolecular interaction between the two fragments of the reacting species is obtained. This result will become the clue to the interesting problem whether the vibrational motion affects the electromagnetic interaction or not.

Appendix to Part II

Intermolecular Force Originated in Vibronic Coupling

Recently, it has been pointed out that the long-range intermolecular scattering potential can depend somewhat on the vibrational state of the constituent molecules.[1] In this respect, it is interesting to discuss whether the nuclear motions affect to induce the intermolecular interaction or not.

The most universal intermolecular interaction is the dispersion force which had been studied by London in 1930.[2-4] The dispersion force is brought about by the virtual excitation of electrons which induces the instantaneous dipole moment. The London type intermolecular potential depends on the separation R between the two molecules as R^{-6}. The correction to the London force was studied in the framework of the non-relativistic quantum electrodynamics[5,6] by Casimir and Polder.[7] Their theory takes explicitly account of the finite speed of the propagation of the electromagnetic interaction. Though the validity of the London theory is restricted in the case where the intermolecular distance R is much smaller than the wavelength characteristic of the electronic transition,[8-9] the theory of Casimir and Polder taking into account of the

retardation effect does not suffer from such disadvantages. The Casimir-Polder dispersion energy has characteristic R^{-7} dependency which is the replacement of the old London R^{-6} energy. The total van der Waals interaction potential of the non-polar molecule is the sum of the Slater exchange repulsion potential[10] and the dispersion energy. The unified treatment of the exchange repulsion energy and the dispersion energy was studied variationally.[3,4,11,12] The most accurate calculation of the London type dispersion energy which does not depend on the multipolar expansion[13] within the Unsöld approximation and the clamped nuclei model was studied.[14]

All these theories do not take into account of the nuclear motions. The nuclear motions, especially the nonadiabatic effects accompanying them are possible to induce the dipole moments which are the origin of the vibrationally induced intermolecular force. This will be clarified in this paper in the framework of the London type treatment and the Unsöld approximation. The interatomic force between the two hydrogen atoms is studied for the ends, because the system already has the most essential physics of the intermolecular force.

First, the interatomic interaction between the two hydrogen atoms induced by the molecular vibration is studied. The homonuclear diatomic system has only one vibrational mode, which is the totally symmetric. The coordinate system adopted

is depicted in Fig.1. The center of mass is fixed on the origin. The perturbation theory is used to describe the interaction.

The zero-th order Hamiltonian is given as the sum of the Hamiltonian of the two separated atoms in the clamped nuclei limit;

$$H_0=-(1/2)(\partial^2/\partial x_1^2+\partial^2/\partial y_1^2+\partial^2/\partial z_1^2)-(1/r_{1A})$$
$$-(1/2)(\partial^2/\partial x_2^2+\partial^2/\partial y_2^2+\partial^2/\partial z_2^2)-(1/r_{2B}), \qquad (1)$$

where the atomic unit is used, $x_i, y_i,$ and z_i denote the x, y, and z coordinate variables of the i-th electron, respectively, and r_{1A} and r_{2B} denote the distance between the A nucleus and the first electron, and the distance between the B nucleus and the second electron, respectively. The perturbative Hamiltonian is then given by the sum of the kinetic energy of nuclei and the Coulomb potential between the two separated atoms as follows;

$$\acute{H}=-(4/M)(\partial^2/\partial R^2)+1/R-1/r_{1B}-1/r_{2A}+1/r_{12}, \qquad (2)$$

where M, R, r_{1B}, r_{2A}, and r_{12} denote the mass of a hydrogen atom, interatomic distance, the distance between the B nucleus and the first electron, the distance between the A nucleus and the second electron, and the distance between the two electrons, respectively. For the long range interatomic distance we may use the following approximation to the perturbative Hamiltonian $\acute{H}$;

$$\acute{H}\sim-(4/M)(\partial^2/\partial R^2)-(1/R^3)(2z_1z_2-x_1x_2-y_1y_2). \qquad (3)$$

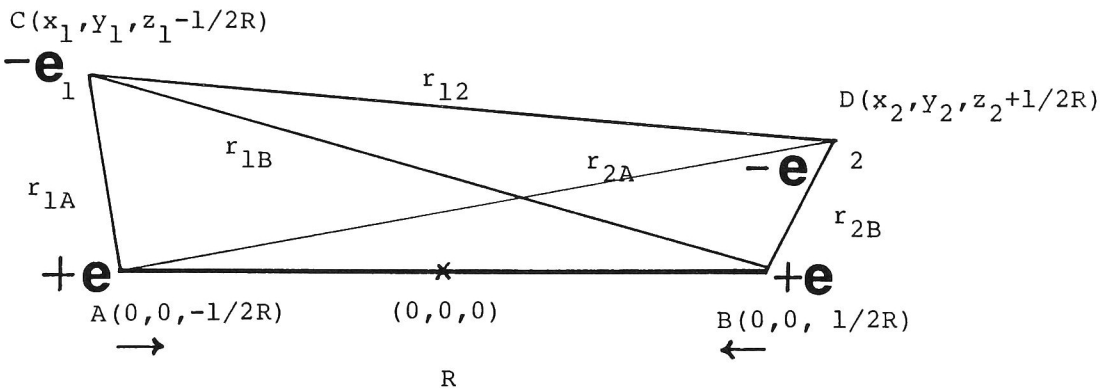

Fig. 1. The coordinate system used for the vibrationally induced interaction.

The higher order corrections[13] to the multipolar expansion will provide the more accurate value than the original London's treatment, as Eq.(3). The zero-th order wavefunction will be the Hartree product of the 1s hydrogen wavefunctions of the two hydrogen atoms $\psi_{1s}(r_{1A})$ and $\psi_{1s}(r_{2B})$ multiplied by the nuclear wavefunction φ_{nuc} ;

$$\Psi_0=\psi_{1s}(r_{1A})\psi_{1s}(r_{2B})\varphi_{nuc}\,. \tag{4}$$

The first order correction to the total energy is given as follows;

$$\begin{aligned} E^{(1)} &= \langle \Psi_0 \mid \acute{H} \mid \Psi_0 \rangle \\ &= \{ -(4/M)\,\partial^2/\partial R^2 \}_n \\ &+ \{ (4/M) \langle \partial\psi_{1s}/\partial R \mid \partial\psi_{1s}/\partial R \rangle \}_n , \end{aligned} \tag{5}$$

where $\{\ \}_n$ denotes the following operation;

$$\{\ \}_n \equiv \int dQ \varphi_{nuc}{}^{*} \varphi_{nuc} \cdot , \tag{6}$$

where Q denotes a collective coordinate for the nuclear motions. The first and second term of the right hand side of the Eq.(5) denote the kinetic energy of nuclei and the nonadiabatic energy between the electronic and nuclear motions, respectively. The second order correction to the total energy is given according to the Unsöld approximation as follows;

$$\begin{aligned} E^{(2)} &= \sum_{k\neq 0} \frac{\acute{H}_{0k}\acute{H}_{k0}}{E_0 - E_k} \\ &\sim -(1/2I)(\acute{H}^2)_{00} + (1/2I)\{(\acute{H})_{00}\}^2 , \end{aligned} \tag{7}$$

where E_0 and E_k are the ground and the k-th excited state

energy of the zero-th order Hamiltonian, i.e. the two hydrogen atoms, and I is the ionization potential of a hydrogen atom. The concrete form of $\acute{H}_{ij}$ and $(\acute{H}^2)_{00}$ are given as follows;

$$\acute{H}_{ij}=\langle \Psi_i \mid \acute{H}\Psi_j \rangle , \tag{8.a}$$

$$(\acute{H}^2)_{00}=\langle \Psi_0 \mid \acute{H}^2\Psi_0 \rangle , \tag{8.b}$$

where Ψ_i is the i-th electronically excited state wavefunction. The second order correction is therefore approximated to be;

$$\begin{aligned} E^{(2)} \sim & (1/2I)\{ \mid \langle \Psi_0 \mid -(4/M)(\partial^2/\partial R^2)\Psi_0 \rangle \mid^2 \\ & -\langle \Psi_0 \mid \{(-4/M)(\partial^2/\partial R^2)\}^2 \cdot \Psi_0 \rangle \} \\ & -(1/2I)\left[(2/3)(\overline{r_1}^2 \overline{r_2}^2/R^6) \right]_n \\ & -(1/2I)\langle \Psi_0 \mid -(4/M)(\partial^2/\partial R^2) \\ & \cdot \{-(1/R^3)(2z_1z_2-x_1x_2-y_1y_2)\}\Psi_0 \rangle \\ & -(1/2I)\langle \Psi_0 \mid \{-(1/R^3)(2z_1z_2-x_1x_2-y_1y_2)\} \\ & \times \{-(4/M)\}\ (\partial^2/\partial R^2) \cdot \Psi_0 \rangle . \end{aligned} \tag{9}$$

The first term of the right hand side of the Eq.(9) expresses the fluctuation of the kinetic energy of nuclear motions. The second term expresses the usual London potential averaged over the nuclear motions, where $\overline{r_1}^2$ and $\overline{r_2}^2$ are the averaged value of r_1^2 and r_2^2 over the electronic motions. The third and fourth terms of the right hand side of Eq.(9) each express the vibrationally induced interatomic interaction energies. The interaction is introduced through the nonadiabatic effect. The third term of the right hand side of Eq.(9) is given concretely as follows;

$$-(1/2I)\langle\Psi_0|\{-(4/M)\}(\partial^2/\partial R^2)$$
$$\cdot\{-(1/R^3)(2z_1z_2-x_1x_2-y_1y_2)\}\Psi_0\rangle$$
$$=(2/I\times M)\left[(1/R^3)(4P^2+2P+1)\right]_n, \tag{10}$$

where P denotes the following integral for the electronic motion;

$$P=\int\psi^*_{1s}(r_{1A})z_1(\partial\psi_{1s}(r_{1A})/\partial R)d\tau_1, \tag{11}$$

where $d\tau_1$ denotes the volume element for the electronic motion. The fourth term is given concretely as follows;

$$-(1/2I)\langle\Psi_0|\{-(1/R^3)\cdot(2z_1z_2-x_1x_2-y_1y_2)\}$$
$$\times\{-(4/M)(\partial^2/\partial R^2)\}\cdot\Psi_0\rangle$$
$$=(8/I\times M)\left[(1/R^3)P^2\right]_n. \tag{12}$$

The fourth term is positive definite. The value of P is $-(1/4)$, on account of the spherical symmetry.

The second order correction to the total energy is the sum of the fluctuation of the kinetic energy of the nuclear motions $\langle\Delta E_{kin}{}^2\rangle$, the London dispersion energy E_{disp}, and the vibrationally induced intermolecular interaction energy $E_{induced}$;

$$E^{(2)}\sim\langle\Delta E_{kin}{}^2\rangle+E_{disp}+E_{induced}, \tag{13}$$

where

$$\langle\Delta E_{kin}{}^2\rangle=(1/2I)\{|\langle\Psi_0|\{-(4/M)\}(\partial^2/\partial R^2)\Psi_0\rangle|^2$$
$$-\langle\Psi_0|\{-(4/M)(\partial^2/\partial R^2)\}^2\Psi_0\rangle\}, \tag{14}$$

$$E_{disp}=-(1/2I)\left[2/3\cdot(\overline{r_1}^2\overline{r_2}^2/R^6)\right]_n, \tag{15}$$

and

$$E_{induced}=(2/I\times M)\left[(1/R^3)\right]_n. \tag{16}$$

Though the London dispersion energy is attractive and has the characteristic R^{-6} dependency, the vibrationally induced interatomic interaction energy is repulsive and has the R^{-3} dependency. It should be noted that on account of the characteristic R^{-3} dependency, the overwhelming magnitude of the mass of nucleus is cancelled out at the large separation between the two atoms. Then the vibrationally induced intermolecular interaction has the comparable magnitude with that of the London dispersion energy. At $R \sim 5.0$ au the magnitude of the vibrationally induced interatomic interaction energy is ca. 1/20 of that of the London dispersion energy, and at $R \sim 14.0$ au the magnitude of the vibrationally induced interatomic interaction energy exceeds that of the dispersion energy, then the total interatomic interaction is repulsive at the large separation, if the kinetic energy of the vibrational motion is taken into account. This will be clearly read from Table 1. Thus the vibrationally induced interatomic interaction cannot be neglected at the large separation, though the overall description of the interaction energy beyond the separation of the characteristic electronic transition wavelength needs to take into account of the retardation effect, which would be interesting.

The essential physics of the vibrationally induced interatomic interaction can be explained in terms of the nonadiabaticity between the electronic motions and the nuclear

Table 1. The energy[a] of the dispersion interaction and the vibrationally induced repulsive interaction at some separations.[a]

R	5.0	10.0	15.0
E_{disp}[b]	-3.887×10^{-4}	-6.005×10^{-6}	-5.272×10^{-7}
$E_{induced}$[b]	1.744×10^{-5}	2.180×10^{-6}	6.459×10^{-7}

[a] All the numerical values are denoted in the atomic unit.

[b] E_{disp} denotes the dispersion energy given by Eq.(15), and $E_{induced}$ denotes the vibrationally induced intermolecular interaction energy given by Eq.(16).

motions and this is schematically drawn in Fig.2(a). When the system vibrates nonadiabatically, the dipole moments which have opposite directions are induced. These instantaneous dipole moments may have the repulsive dipole-dipole interaction. This simple elucidation may give arise to the idea that the nonadiabatic translational motion induces the dipole moments which have the same directions and hence they induce the attractive interaction. This is schematically shown in Fig.2(b).

If the box-normalized translational wavefunction is used, the interatomic interaction induced by the nonadiabatic translational motion can be investigated theoretically. The coordinate system adopted is shown in Fig. 3. The zero-th order Hamiltonian and the wavefunction is formally the same with Eqs.(1) and (4). The perturbative Hamiltonian in this case is given at the asymptotic separation as follows;

$$\acute{H}\sim-(1/M)(\partial^2/\partial\xi^2)-(1/R^3)(2z_1z_2-x_1x_2-y_1y_2), \tag{17}$$

where the first and the second terms express the kinetic energy of the translational motion and the long-range Coulomb interaction, respectively. The first order correction to the total energy is the sum of the kinetic energy of the translational motion and the nonadiabatic energy;

$$E^{(1)}=\left[-(1/M)(\partial^2/\partial\xi^2)\right]_n + \left[(1/M)\langle\partial\psi_{1s}/\partial\xi\,|\,\partial\psi_{1s}/\partial\xi\rangle\right]_n \tag{18}$$

The second order correction to the total energy is given in

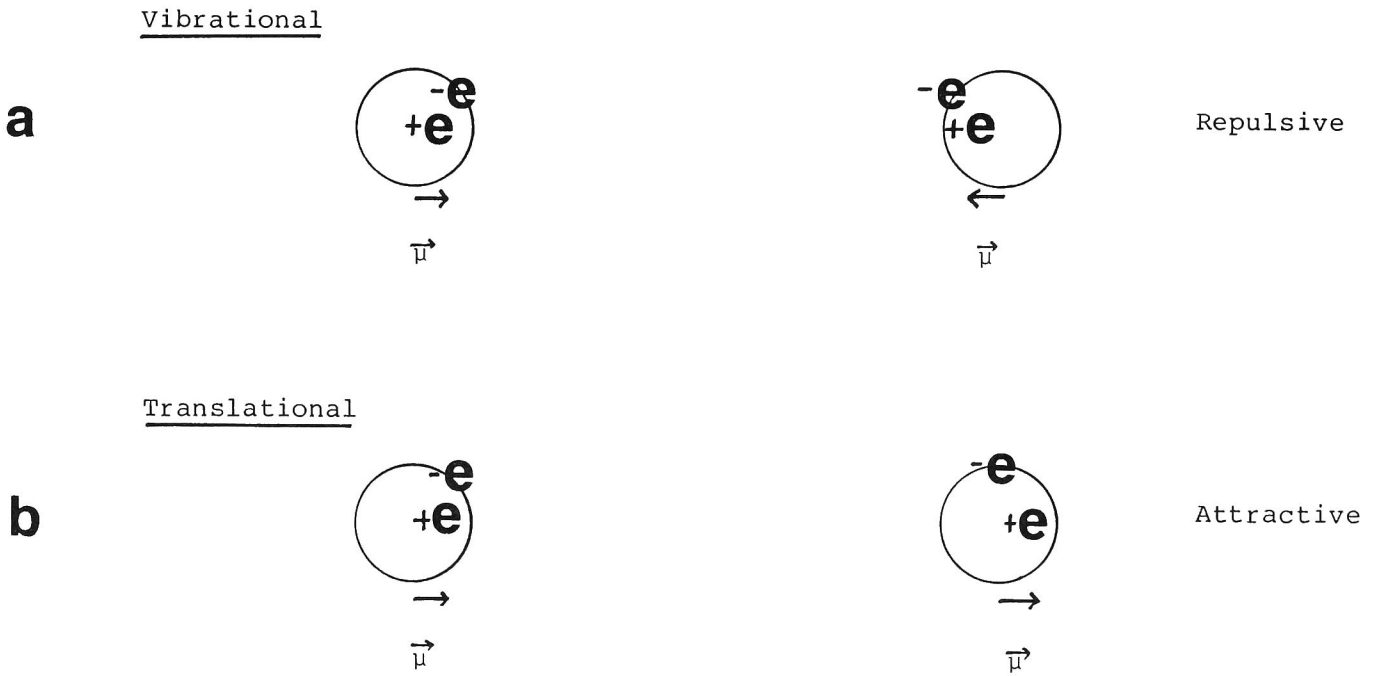

Fig. 2. The schematic representaions of the instantaneous dipole moments induced by the nonadiabatic motions of electrons and nuclei, (a) is for the vibrational motion of the nuclei, and (b) is for the translational motion of the nuclei. Arrows denote the directions of the instantaneous dipole moments denoted by $\vec{\mu}$ for each.

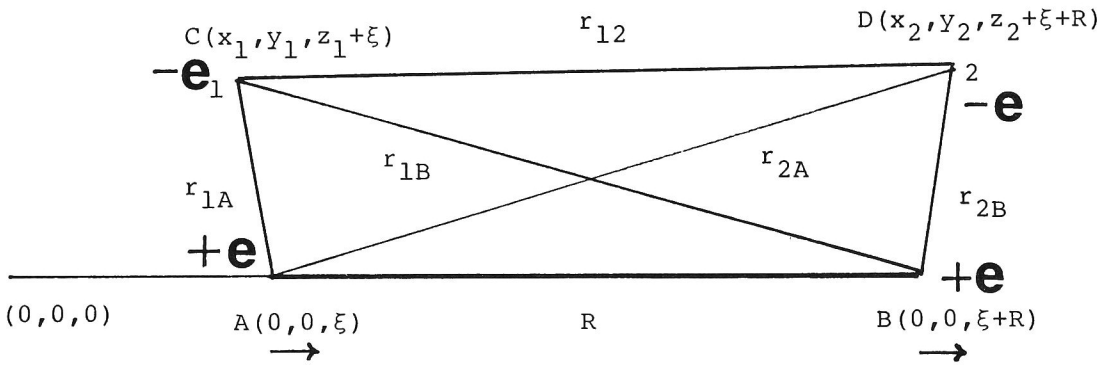

Fig. 3. The coordinate system used for the interaction induced by the translational motion.

the Unsöld approximation as the sum of the fluctuation of the kinetic energy of the translational motion $\langle \Delta E_{kin}^2 \rangle$, the London dispersion energy E_{disp}, and the translationally induced interatomic interaction energy $E_{induced}$;

$$E^{(2)} \sim \langle \Delta E_{kin}^2 \rangle + E_{disp} + E_{induced}, \tag{19}$$

where

$$\langle \Delta E_{kin}^2 \rangle = (1/2I) \{ | \langle \Psi_0 | \{ -(1/M) \} (\partial^2/\partial \xi^2) \Psi_0 \rangle |^2 - \langle \Psi_0 | \{ -(1/M) (\partial^2/\partial \xi^2) \}^2 \Psi_0 \rangle \}, \tag{20}$$

E_{disp} is the same with the Eq.(14), and

$$E_{induced} = -(2/I \times M) [(1/R^3)]_n. \tag{21}$$

Then the interatomic interaction induced by the nonadiabatic translational motion is attractive and it has the characteristic R^{-3} dependency. It is interesting to point out that the vibrationally induced intermolecular interaction potential and the intermolecular interaction potential induced by the translational motion have the same absolute value at the same separation, but have opposite signs. This attractive interaction induced by the translational motion will be interesting in the light of the Cooper paring of electrons and the Frölich mechanism[15] in the theory of the low dimensional superconductivity where the higher critical temperature is actively discussed. The longitudinal phonon plays an important role in the Bose condensation of the Cooper pair of electrons. The apparently different effects between the vibrational and the translational motions on the interatomic interaction are

interesting. Of course, the higher order polarizability should be discussed for the discussion.

It has been demonstrated that the intermolecular dispersion force depends on the nuclear motions. The dispersion force which has been explicitly considered in this study is universal; all the molecules have the intermolecular dispersion force.[17] Thus the intermolecular force must depend on the state of the nuclear motions. The novel intermolecular interaction has the characteristic R^{-3} dependency and hence it cannot be neglected at the large separation, is spite of the overwhelming magnitude of the mass of nucleus. The vibrational and the translational motion of the nuclei affect quite differently on the usual intermolecular interaction. The vibrationally induced intermolecular force is repulsive. The intermolecular force induced by the translational motion is attractive. These distinct roles of the nuclear motions will be interesting in the condensed matter physics. The importance of the long-range interaction in the condensed matter has been pointed out.[9] The analysis presented here can be easily extended to the *He-He* system, where the superfluidity of ^3He is actively discussed[16] along with the mechanism of Cooper paring. The usual van der Waals force is assumed there. The novel intermolecular forces are induced by the nuclear motions and result in the modification of the nuclear motions. Then these forces may be interesting in the self-organization of

the molecule where the nonlinear Schrödinger equation[17] is actively discussed. Also it will be important to study the universal nature of the novel intermolecular interaction for the general molecular system.[18]

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PART III

The Dynamic Aspects of the Occupation Number of the Electron Orbital

Chapter 1

Introduction

In the study of electronic processes accompanying chemical reaction on the basis of the orbital concept, the Born-Oppenheimer adiabatic approximation which neglects the correlation between the motions of electrons and nuclei is the starting point, though the general extension of the dynamic electron orbitals obtained in part I of this thesis to the scattering problem, if possible, is more desirable. The change of electronic structure accompanying a chemical reaction is traced through the parametric change of a nuclear configuration. The reaction coordinate, especially the Intrinsic Reaction Coordinate(IRC) is usually used as the collective coordinate for the nuclear motions, and is a generalized normal vibration for the large amplitude molecular vibration. The evolution of the electron orbitals along the reaction coordinate raises the problem that the two sets of electron orbitals at two neighboring points on the reaction coordinate do not have a strict correspondence at all. This comes from the fact that the two sets of electron orbitals are determined independently at the two distinct points on the reaction coordinate. This inhibits a natural interpretation of a smooth electron rearrangement accompanying the chemical reaction. If one carries out a truncated configuration

interaction calculation or another calculation that is aimed at incorporating electron correlation without the full use of the functional space of the basis atomic orbitals, and if one makes natural orbitals after the calculation to preserve the one electron orbital concept, the resultant natural orbitals may reveal the disadvantage mentioned above, owing to the fact that different active space may be used at the two distinct points on the reaction coordinate for the calculation. Apart from this actual difficulty, it would be nice to obtain a set of electron orbitals which retain the feature of adiabatic continuity, because the deviations from adiabatic continuity can then be discussed on the same footing. A suitable parameter for the nuclear configuration will be the IRC, because it is defined as a steepest descent path of the potential energy surface of the nuclei passing through a critical point of the surface. It represents the locus of the nuclear motion when it is constrained to have infinitesimal velocity. An electron orbital which changes as little as possible as it evolves along the IRC will be an electron orbital which has the feature of adiabatic continuity. This electron orbital is defined so as to introduce the IRC concept into the manifolds of electron orbitals along the IRC. The deviation may be traced by using a integrated line element of a trajectory of the nuclear motion as the parameter.

In chapter 2 of this part (J. Chem. Phys.,

83,6334(1985)), a one-to-one correspondence between the two sets of the electron orbitals separated by an infinitesimal distance on the reaction coordinate is introduced using the criterion of the overlap integrals between them. The Amos-Hall corresponding orbital transformation method is used at that time. By taking the limit as the infinitesimal distance tends to zero, a set of unique electron orbitals which present the general feature of adiabatic continuity is obtained. If we trace the transformed orbitals along the IRC, the smooth electron rearrangements accompanying the chemical reaction can be studied. Indeed, the occupation number of the transformed electron orbital can be defined naturally by representing the diagonal element of the first order density matrix using the transformed orbitals. The change of the occupation numbers along the IRC represent the smooth electron rearrangement. The electronic process of the radical reaction; CH_3 + HF -> CH_4 + F , is studied through the analysis of the transformed electron orbitals, along with the analysis of the dynamic electron transfer accompanying the motion of the wavepacket along the IRC discussed in part II of this thesis, and the usual analysis of the canonical orbitals. The new feature of characteristic electronic processes during the reaction is clarified on the basis of the transformed electron orbitals and their occupation numbers.

In chapter 3 of this part (Synthetic Metal, in press),

electron transport between two chains of polyacetylene and between the dopant molecule and polyacetylene induced by molecular vibration are studied by analyzing the transformed electron orbitals and the dynamic electron transfer. The locally isomorphic chemical reaction analogue systems; CH_3 + CH_4 -> C_4 + CH_3 and CH_3 + HF -> CH_4 + F are used for this study. The characteristic change of the correlation diagram of the occupation numbers and the orbital energies of the transformed electron orbitals is obtained. The orbital energies can be defined naturally by representing the diagonal element of the Fock matrix of the canonical orbital by using the transformed orbitals. The mode specific feature of the electron transport is also discussed.

In chapter 4 of this part (to be submitted for publication), the electronic flexibility of the cyclopropenyl radical to molecular vibration is studied to discuss the possibility of the channel switching of the soliton valve which is one of the molecular devices proposed by Carter. The area of the cell structure of the nonrigid cyclopropenyl radical is discussed in this context. If the change of the occupation numbers of the transformed orbitals is large, the electron can be said to be flexible against molecular vibration and hence the area of the electronic cell can also be said to be small, and vice versa. A derivative expression of the rearrangement operator of the transformed electron

orbitals is obtained to discuss the analytical structure of the rearrangement operator. The rearrangement operator with the derivative expression is shown to have a close relation with the nonadiabatic kinetic coupling of the motions of electrons and nuclei. It is interesting to remember that the close quantum mechanical relation between the displacement operator and the momemtum operator discussed in the text book of quantum mechanics written by Dirac.

The rearrangement of electrons affected by the local quantum fluctuation accompanying the nuclear motion along the IRC is also discussed. Finally, the conclusions obtained from chapter 2 to chapter 4 are discussed and summarized in chapter 5 of this part.

Chapter 2

Morphology of Dynamic Electron Transfer Characteristic of Chemical Reaction Dynamics

I. INTRODUCTION

The dynamics of molecular vibrations during a chemical reaction have received much attention in the case of highly energy-resolved experiments involving molecules.[1] Especially, the change of reactivities accompanying excitations of molecular vibrations in laser chemistry experiments is interesting with respect to inter-, and intramolecular energy transfer processes. The significant role of molecular vibrations in chemical reactions has recently been demonstrated.[2]

Traditional studies on the dynamic behaviour of nonrigid molecules have been achieved in the most case, on the basis of the Born-Oppenheimer(BO) adiabatic approximation. In the BO approximation, the degrees of freedom of the motion of the electrons and nuclei are treated in quite distinct stages. Thus the BO approximation is not sufficient in the case in which the couplings between nuclear motion and electronic motion are large. In this respect, many studies which go beyond the BO approximation have been performed,[3-9] and the

concept of the dynamic structure of a molecule has received much attention.[10,11] Above all, the nonadiabatic coupling between molecular vibration and electronic structure is considered to be the fundamental clue in the field of chemical physics, to explain e.g. the radiationless transition process in the condensed phase, electric conductivity in organic and inorganic materials, and electron and proton transfer reactions in biological systems.[12] Moreover, in terms of molecular quantum fluid dynamics,[13] the analysis of the dynamic effect of the nuclear motion on the electronic motion may elucidate a new interpretation of the elementary chemical reaction processes.

In previous parts, we developed the dynamic analysis of the electronic structure of molecules in the course of molecular vibration.[14,15] This analysis incorporates the dynamics of nuclear motion into the electron orbital, then it includes the nonadiabatic effect, and the zero point vibrational effect on the electronic structure. Theoretical and numerical analysis of the novel additive property of the electron density which reflects the quantum effect of molecular vibration are also achieved, and we concluded that this effect is sufficiently large enough to be observed by experimental study. Thus it has been emphasized that the quantum effect of molecular vibration is largely reflected in the electronic charge distribution. Moreover, by solving the

dynamic Fock equation, one can study the reaction dynamics including the electronic transition process.

From this point of view, the dynamical study of a chemical reaction should be analyzed with consideration to the quantum effect of the molecular vibration on the electronic state and the kinetic coupling of molecular vibration with electronic structure. Though the most rigorous treatment should be based on a fully quantum mechanical description,[4-6] the above mentioned analysis also provides us with a novel concept of the "dynamic electron transfer"[14,15] which accompanies the reaction process.

The electron orbitals thus obtained at two different points of the reaction coordinate are not isomorphic, and it is therefore interesting to rearrange the electron orbitals so as to make them isomorphic. Then it is possible to discuss the electronic process accompanying the reaction in terms of the transition process of the occupation number on a definite set of the electron orbital manifold. The new rearrangement operator which can be obtained by using the displacement vector of the degree of freedom of the nuclear motion will be discussed in the Section II. In this chapter, we demonstrate the intrinsic morphology of the electron and spin transfer characteristic of chemical reaction dynamics in the following radical abstraction reaction

$$CH_3 + HF \rightarrow CH_4 + F \qquad (I)$$

We used the HONDOG program[16] to determine the reaction coordinate. Some other calculations were performed by the Gaussian80 program.[17] The dynamic electron density and the transformed electron orbital were calculated by Gaussian80 and extra subroutines which we wrote. We used adiabatic UHF molecular orbitals[18] at the 4-31G[19] level to determine the natural orbitals $\{\psi_k(0)\}$ and $\{\psi_k(1)\}$ in Eq.(5).

II. THE MORPHOLOGY OF ISOMORPHIC ELECTRON ORBITALS ALONG THE REACTION COORDINATE

The dynamic electron orbitals which are solutions of the dynamic Fock equation Eq.(11) at two different points of the reaction coordinate do not have a definite criterion for their isomorphic equivalency. Therefore it is interesting to introduce a criterion, which can be used to transform the electron orbitals. This enables us to analyze the dynamic rearrangement of electron orbitals accompanying the reaction process as the change of the occupation numbers of the electron orbitals. This criterion is a development of the well-known Amos-Hall corresponding orbitals.[20,21]

The natural orbitals[22] $\psi_i(0)$ and $\psi_i(1)$ at two distinct points s_0 and s_1 of the reaction coordinate have overlap integral S_{ij};

$$S_{ij}=\langle \psi_i(0) \mid \psi_j(1) \rangle \ . \qquad (1)$$

This situation is illustrated schematically in Fig.1. A certain number of natural orbitals at s_1 have non-zero overlap integrals with a natural orbital at s_0 and there is no definite criterion for isomorphic equivalency between the two natural orbital manifolds at s_0 and s_1. Defining the following Hermitian matrix $||R_{ij}||$ as the rearrangement operator;

$$R_{ij} = \sum_m S_{mi}^* S_{mj} \quad , \tag{2.a}$$

$$R_{ij} = R_{ji}^* \quad , \tag{2.b}$$

the eigenvalue and eigenvector of the operator are denoted as γ_k and U_{ik} ,respectively;

$$\sum_j R_{ij} U_{jk} = U_{ik} \gamma_k \quad , \tag{3}$$

and the eigenvector U_{ik} is normalized so that;

$$\sum_i U_{ik}^* U_{in} = \delta_{kn} \quad . \tag{4}$$

the transformed electron orbitals $\tilde{\psi}_k(0)$ and $\tilde{\psi}_k(1)$ are obtained as follows;

$$\tilde{\psi}_k(1) = \sum_i U_{ik} \psi_i(1) \quad , \tag{5.a}$$

$$\tilde{\psi}_k(0) = (1/\sqrt{\gamma_k}) \sum_j \sum_m S_{mj} U_{jk} \psi_m(0) \quad . \tag{5.b}$$

The overlap matrix of the two sets of transformed orbitals $\{\tilde{\psi}_k(1)\}$ $\{\tilde{\psi}_k(0)\}$ is diagonal so that the following

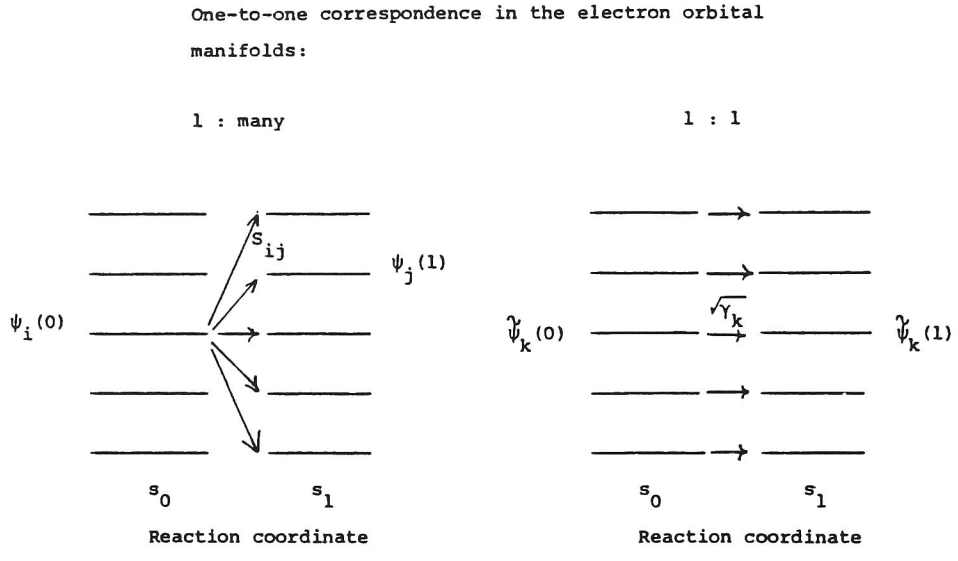

FIG. 1. Depiction of the isomorphism between the two electron orbital manifolds at different points of the reaction coordinate. Natural orbitals at different nuclear configurations generally have a nondiagonal overlap matrix S_{ij}, and hence do not have a definite criterion for correspondence. Transformed orbitals at different points of the reaction coordinate obtained by Eq. (5) satisfy Eq. (6), and have the diagonal overlap matrix $\sqrt{\gamma_k}\,\delta_{kn}$ and hence have a definite criterion for correspondence.

orthonormality relations are obtained;

$$\langle \tilde{\psi}_k(0) | \tilde{\psi}_n(0) \rangle = \delta_{kn} \ , \tag{6.a}$$

$$\langle \tilde{\psi}_k(1) | \tilde{\psi}_n(1) \rangle = \delta_{kn} \ , \tag{6.b}$$

$$\langle \tilde{\psi}_k(0) | \tilde{\psi}_n(1) \rangle = \sqrt{\gamma_k}\,\delta_{kn} \ . \tag{6.c}$$

As $s_1 \rightarrow s_0$, $\{\tilde{\psi}_k(1)\} \rightarrow \{\tilde{\psi}_k(0)\}$ and let s_0 be varied as we move along the chemical reaction coordinate; therefore a new set of electron orbitals which is uniquely determined all over the reaction process can be obtained.

The electron density functions $\rho(0)$ and $\rho(1)$ at s_0 and s_1 can be written in terms of the natural orbitals $\{\psi_i(0)\}$ and $\{\psi_i(1)\}$ as follows;

$$\rho(0) = \sum_i \nu_i(0)\psi_i(0)^*\psi_i(0) \ , \tag{7.a}$$

$$\rho(1) = \sum_i \nu_i(1)\psi_i(1)^*\psi_i(1) \ , \tag{7.b}$$

where $\nu_i(0)$ and $\nu_i(1)$ are the occupation numbers of the natural orbitals $\psi_i(0)$ and $\psi_i(1)$, respectively. Moreover, $\rho(0)$ and $\rho(1)$ can be also written in terms of $\{\psi_i(0)\}$ and $\{\psi_i(1)\}$ as follows;

$$\rho(0) = \sum_m \nu_m(0) \sum_i \sum_k \sum_j \sum_n (1/\sqrt{\gamma_k}) S_{mi} U_{ik}$$

$$\times (1/\sqrt{\gamma_n}) S_{mj}^* U_{jn}^* \tilde{\psi}_k(0)^* \tilde{\psi}_n(0) \ , \tag{8.a}$$

$$\rho(1) = \sum_m \nu_m(1) \sum_k \sum_n U_{mk} U_{mn}^* \tilde{\psi}_k(1)^* \tilde{\psi}_n(1) \ . \tag{8.b}$$

We define the occupation numbers of the electron orbitals $\tilde{\psi}_n(0)$ and $\tilde{\psi}_n(1)$ as follows;

$$\tilde{\nu}_n(0) = (1/\gamma_n)\sum_m \nu_m(0)\sum_i\sum_j S_{mi}S_{mj}^* U_{in}U_{jn}^* \ , \tag{9.a}$$

$$\tilde{\nu}_n(1) = \sum_m \nu_m(1)U_{mn}U_{mn}^* \ . \tag{9.b}$$

These are the terms in Eq.(8.a) and (8.b) for which k=n. Again, as $s_1 \rightarrow s_0$, $\tilde{\nu}_n(1) \rightarrow \tilde{\nu}_n(0)$ and let s_0 be varied as we move along the chemical reaction coordinate; we can determine the change of occupation number uniquely along the reaction coordinate. The rearrangements of electrons within the electron orbital manifold are estimated by the change of the occupation numbers of the transformed electron orbitals and the off-diagonal ($k \neq n$) terms of the density matrix. Thus we can introduce the isomorphism of electron orbital manifolds accompanying the reaction process. Furthermore, we can demonstrate the electronic process of the chemical reaction with respect to the change of occupation numbers of the electron orbitals. This establishes the morphology of the electron transfer characteristic of a chemical reaction.

III. ADIABATIC AND CANONICAL ELECTRONIC PROCESSES IN THE RADICAL REACTION; $CH_3 + HF \rightarrow CH_4 + F$

A radical reaction is known to be such that it is not

easily affected by its environment. Hence many studies concerning the electronic process of such reactions have been performed theoretically.[23] Not only electronic donation from the substrate fragment to the radical fragment but also electronic back donation from the radical fragment to the substrate fragment is considered to be important interaction which promotes the chemical reaction. The donation of a β-spin electron from the highest occupied molecular orbital(HOMO)[24] of the substrate molecule to the singly occupied molecular orbital(SOMO)[24] of the radical molecule, and the back donation of an α-spin electron from the SOMO of the radical molecule to the lowest unoccupied molecular orbital(LUMO)[24] promotes the spin polarization of the old bond in the two fragments and deposits electronic charge in the new bond which is formed. Then, the formation of the new bond is promoted, and these interactions help to weaken the old bond. This is the basic electronic process of the reaction (I), whose energetics has been studied by Sana, Leroy, and Villaveces,[23(b)] as will be clarified in this section using the concept of the intrinsic reaction coordinate(IRC).[25-27]

III.A. Analysis of IRC

The potential energy of the nuclear motion and changes of the geometrical parameters along the intrinsic reaction

coordinate (IRC; s)[25-27] are depicted in Figs.2(a) and 2(b), respectively. The barrier of the potential of the reaction and the exothermicity of the reaction are calculated to be 18.2 and 8.2 kcal/mol, respectively. The zero-point vibrational energy correction improves the barrier and exothermicity to 19.6 and -1.1 kcal/mol, respectively.

From Fig.2(b), the geometrical change accompanying the reaction is characterized as follows; first, from s=-0.4 to s=0.4 the immigrant hydrogen atom moves from the substrate fragment HF to the radical fragment CH_3 while the distance between the C and F atoms remains almost the same. Secondly, the change of the bond angle θ is relatively small in the interval from s=-0.4 to s=0.4. Moreover, the energetic change in the interval from s=-0.4 to s=0.4 is large in comparison with other domains of the reaction coordinate. Thus, this reaction can be said to have the characteristic proton transfer process.

III.B. Analysis of the Canonical Electron Orbital

The change of the charge donation from the substrate fragment to the radical fragment, the charge back donation from the radical fragment to the substrate fragment, and the spin polarization along the reaction coordinate are summarized in Table 1. The donation and backdonation are analyzed

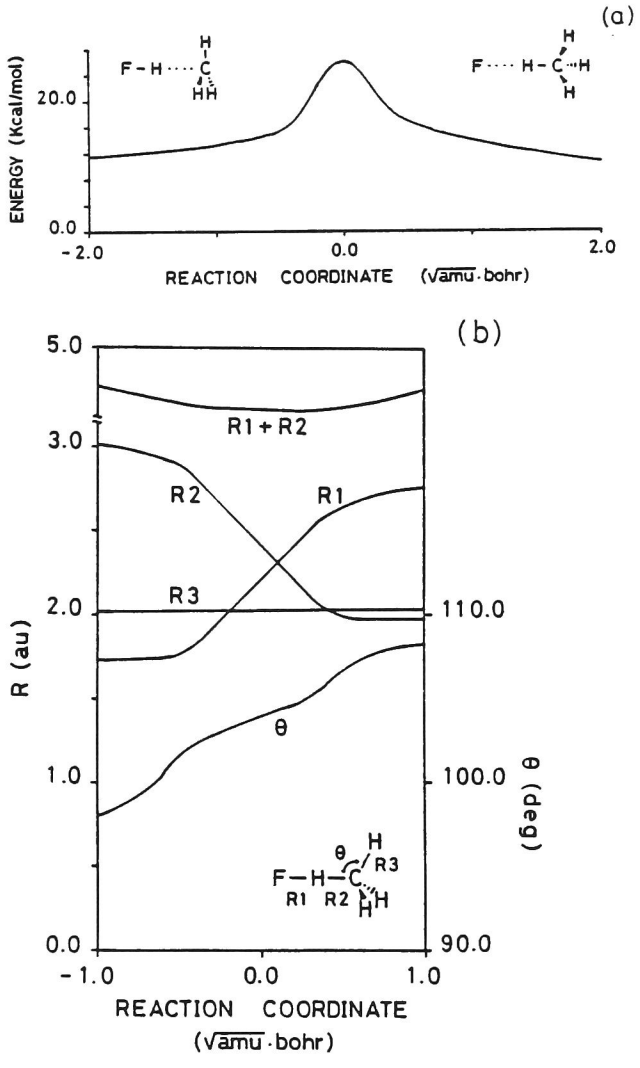

FIG. 2. (a) Potential energy profile, and (b) the changes of bond lengths and bond angle along the IRC. The IRC is depicted in units of $\sqrt{\text{amu}}$ bohr. The transition state is located at the origin and IRC is negative (positive) on the reactant (product) side.

TABLE I. Change of the interaction between the two fragments along the reaction coordinate.

s^a	− 1.0	− 0.8	− 0.6	− 0.4	− 0.2	0.0	0.2
CT[b]	0.039 28	0.041 70	0.044 00	0.052 37	0.092 22	0.191 98	0.343 62
BCT[c]	0.058 06	0.059 62	0.059 97	0.068 58	0.112 48	0.179 88	0.260 81
Spin density							
H	− 0.023 20	− 0.025 18	− 0.025 40	− 0.038 31	− 0.108 40	− 0.189 78	− 0.180 92
F	0.120 52	0.126 50	0.129 36	0.159 27	0.313 08	0.561 59	0.785 36

[a] Intrinsic reaction coordinate, the unit and the location are the same with Fig. 2(a).
[b] The charge donation from the substrate fragment to the radical fragment.
[c] The charge back donation from the radical fragment to the substrate fragment.

quantitatively by utilizing the total changes of the gross orbital charges between isolated systems and complex systems within each fragment. Both the donation and back donation interactions between the two fragments increase as the reaction proceeds. Moreover, rather dominant interaction of backdonation is surmounted by the donation at the saddle point of the potential surface. The spin polarization in the HF fragment increases accompanying the reaction process, and it is especially prominent at s=-0.4. Accordingly, the interval of the reaction coordinate from s=-0.4 to s=0.0 is important, in the electronic process of this reaction. This agrees with the results of the analysis of geometrical parameters along IRC as described in Sec.III-A.

This reaction has a characteristic in that the back donation is the more dominant process during the early stages of the reaction, compared with another similar reaction[23] such as

$$CH_3 + H_2 \rightarrow CH_4 + H \ . \qquad \text{(II)}$$

It is clearly elucidated by the orbital mixing rule. An MO correlation diagram is shown in Fig.3, in which the molecular orbitals of the complex system at s=-1.0 of the reaction coordinate are placed at the middle. The SOMO ψ_{10} consists mainly of the mixture of (1) the antibonding orbital ψ_6 of the HF fragment, and the radical orbital ψ_5 in phase, and (2) the bonding orbital ψ_3 of the HF fragment out of phase. It is

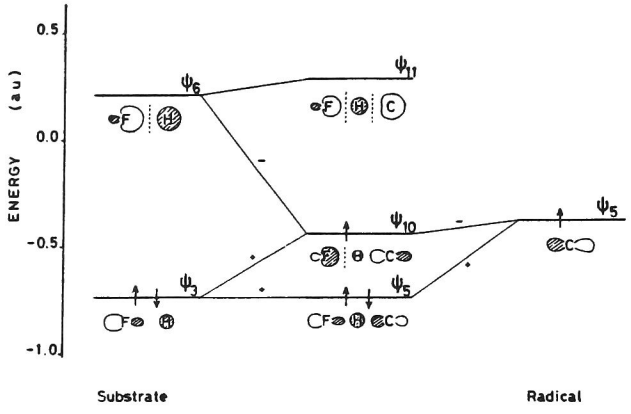

FIG. 3. An MO correlation diagram. Orbital interactions between the two fragments: CH_3 and HF, at $s = -1.0$ on the reaction coordinate. Same (different) signs indicate that the orbitals mix in phase (out of phase).

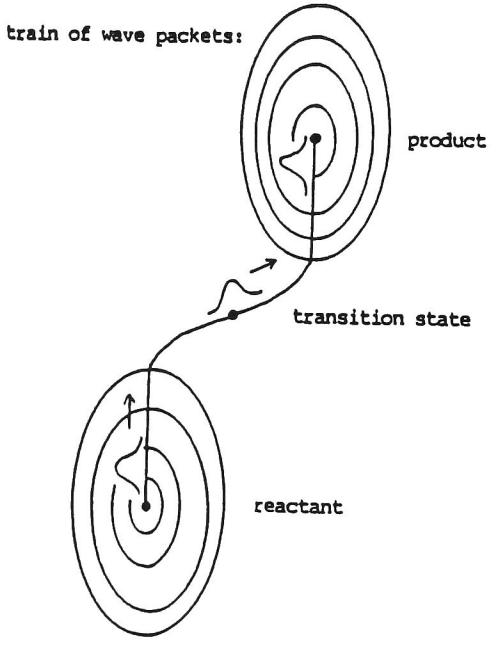

FIG. 4. Schematic representation of the train of wave packets along the reaction coordinate which travels from the reactant cell to the product cell.

found that the contribution of ψ_6 is large, because the nodal point of ψ_{10} stays at the mid-point of the HF fragment, which has ψ_6 character. This shows that the back donation interaction is large in the early stages of the reaction. On the other hand, the orbital mixing of an antibonding orbital of the substrate fragment is small in reaction (II) at s=-1.0, which shows that the back donation interaction is not large at s=-1.0. This result of reaction (II) is quite different from our result in reaction (I), and this difference is characteristic in these two reactions.

IV. MORPHOLOGY OF DYNAMIC ELECTRON TRANSFER ALONG THE REACTION COORDINATE

A full quantum mechanical description of the nuclear motion along the reaction coordinate will not be accomplished in this work. In spite of this, we use the coherently oscillating wavepacket on the reaction coordinate as the nuclear wavefunction. Then the nuclear motion around the center of oscillation is treated quantum mechanically, and hence the neighborhood of the center constitute the domain where the electronic structure of the molecule reflects the dynamics of the nuclei well. Then it is interesting to investigate the correlation of a quantity with respect to the reaction coordinate. The correlation enables us to investigate

the dynamic change of the quantity in the course of the reaction process. We call the correlation of the dynamic electron transfer at successive points on the reaction coordinate the stream of the dynamic electron transfer.[28]

IV-A. The Dynamic Electron Transfer and the Additive Property

We define the following dynamic electron density characterized by the nuclear wavefunction Ψ_{nuc};

$$\langle \rho \rangle = \int \rho \Psi_{nuc}^{*} \Psi_{nuc} dQ \ , \tag{10.a}$$

where Q denotes the normal coordinate.

$$\int \Psi_{nuc}^{*} \Psi_{nuc} dQ = 1 \ , \tag{10.b}$$

Here, ρ is obtained from the set of the dynamic electron orbitals $\{\psi_i\}$ which are solutions of the following dynamic Fock equation;[14,15]

$$\underline{f} \underline{c_i} = \varepsilon_i \underline{c_i} \ , \tag{11.a}$$

$$\underline{f} = \langle \Psi_{nuc} | \underline{F} + \underline{\Delta} | \Psi_{nuc} \rangle \ , \tag{11.b}$$

$$\Delta_{rs} = (1/2) \langle \partial \varphi_r / \partial Q | \partial \varphi_s / \partial Q \rangle$$

$$+ \ (1/2) \sum_{t}^{'} \sum_{u}^{'} \sum_{j}^{occ} c_{tj}^{*} c_{uj}$$

$$\times (\langle \partial \varphi_r / \partial Q | \varphi_s \rangle \langle \varphi_t | \partial \varphi_u / \partial Q \rangle$$

$$+ \langle \partial \varphi_t / \partial Q | \varphi_u \rangle \langle \varphi_r | \partial \varphi_s / \partial Q \rangle$$

$$- \langle \partial \varphi_r / \partial Q | \varphi_u \rangle \langle \varphi_t | \partial \varphi_s / \partial Q \rangle$$

$$-\langle \partial\varphi_t/\partial Q|\varphi_s\rangle\langle\varphi_r|\partial\varphi_u/\partial Q\rangle), \tag{11.c}$$

$$\psi_i = \sum_r \varphi_r c_{ri} \ , \tag{11.d}$$

where $\{\varphi_r\}$ is an orthonormal basis set so that;

$$\langle \Psi_{nuc}|\langle\varphi_r|\varphi_s\rangle|\Psi_{nuc}\rangle = \delta_{rs} \ . \tag{12}$$

If we adopt the harmonic wavefunction as the nuclear wavefunction, the dynamic electron density defined by Eq.(10) approximately satisfies the following additive property;[14,15]

$$\langle\rho\rangle_\nu \sim \rho(0)+(1/2\omega)(\partial^2\rho/\partial Q^2)(0)(\nu+1/2) \ , \tag{13}$$

where, ν and ω stand for the vibrational quantum number and the vibrational frequency, respectively. Eq.(13) implies that if a molecule is vibrationally excited, then the increment of the dynamic electron density is proportional to the difference of the vibrational quantum number. If we adopt a coherently oscillating wavepacket[29] initially centered at $Q=Q_0$ as the nuclear wavefunction;

$$\Psi_{wavepacket} = (\omega/\pi)^{1/4}\exp[-(1/2)\omega(Q-Q_0\cos\omega t)^2$$
$$-i\{(1/2)\omega t+\omega QQ_0\sin\omega t-(1/4)\omega Q_0^2\sin 2\omega t\}] \ , \tag{14}$$

then we have the following dynamic electron density accompanying the coherent motion of the nucleus at the reaction coordinate s;

$$\langle\rho\rangle_{wavepacket} \sim \rho(0;s) + (\partial\rho/\partial Q)(0;s)Q_0\cos\omega t$$

$$+ \ (1/2)(\partial^2\rho/\partial Q^2)(0;s)\{1/(2\omega)+(Q_0\cos\omega t)^2\} \ . \qquad (15)$$

If we take the average of $\Psi_{\text{wavepacket}}$ over one period τ at the stable equilibrium point, then

$$\overline{\langle\rho\rangle}_{wavepacket} \equiv (1/\tau)\int_0^\tau \langle\rho\rangle_{wavepacket}dt$$

$$\sim\rho(0)+(1/2\omega)(\partial^2\rho/\partial Q^2)(0)(\nu_c+1/2) \ , \qquad (16)$$

where τ is given by $2\pi/\omega$ and ν_c is represented by

$$\nu_c = (1/2)\omega Q_0^2 \ . \qquad (17)$$

The dynamic electron transfer accompanying the train of the wavepackets on the reaction coordinate thus satisfies the rigid additive property at the stable point, and therefore the characteristic time accompanying the reaction process is connected smoothly all over the reaction coordinate.[28] The evolution of the wavepacket is schematically represented in Fig.4. The dynamic electron transfer accompanying the multimode molecular vibration is represented within the same approximation of Eq.(13) by

$$\langle\rho\rangle_{\nu_1,\nu_2,\ldots,\nu_a}$$

$$\sim \ \rho(0)+\sum_i(1/2\omega_i)(\partial^2\rho/\partial Q_i^2)(0)(\nu_i+1/2) \ . \qquad (13)$$

This property will be useful for the fully dynamical treatment

of the dynamic electron transfer in polyatomic molecular systems.

IV-B. The Dynamic Electron Current along the Reaction Coordinate

We have shown that nuclear motion in reaction (I) is quite characteristic of the proton transfer process. Moreover the reaction has a prominent electronic process in that the back donation has a large interaction component in the early stages of the reaction. Before analyzing the dynamic electron density, it is interesting to investigate the adiabatic electron density on the reaction coordinate. Figs.5(a) and 5(b) show the adiabatic spin density and the electron density, respectively. From Fig.5(a), it can be seen that the transferred proton brings more β-spin electron density than the hydrogen atom in the methyl radical fragment, though the electron density around the transferred proton is less than that around the hydrogen atom in the methyl radical fragment. This means that the transferred proton atom plays the major role in moving the β-electron which is the electron transferred by the back donation interaction.

Next we analyzed the stream of dynamic electron transfer. Figs.6(a),6(b),6(c),and 6(d) show the dynamic spin density, α-spin electron density, β-spin electron density, and total

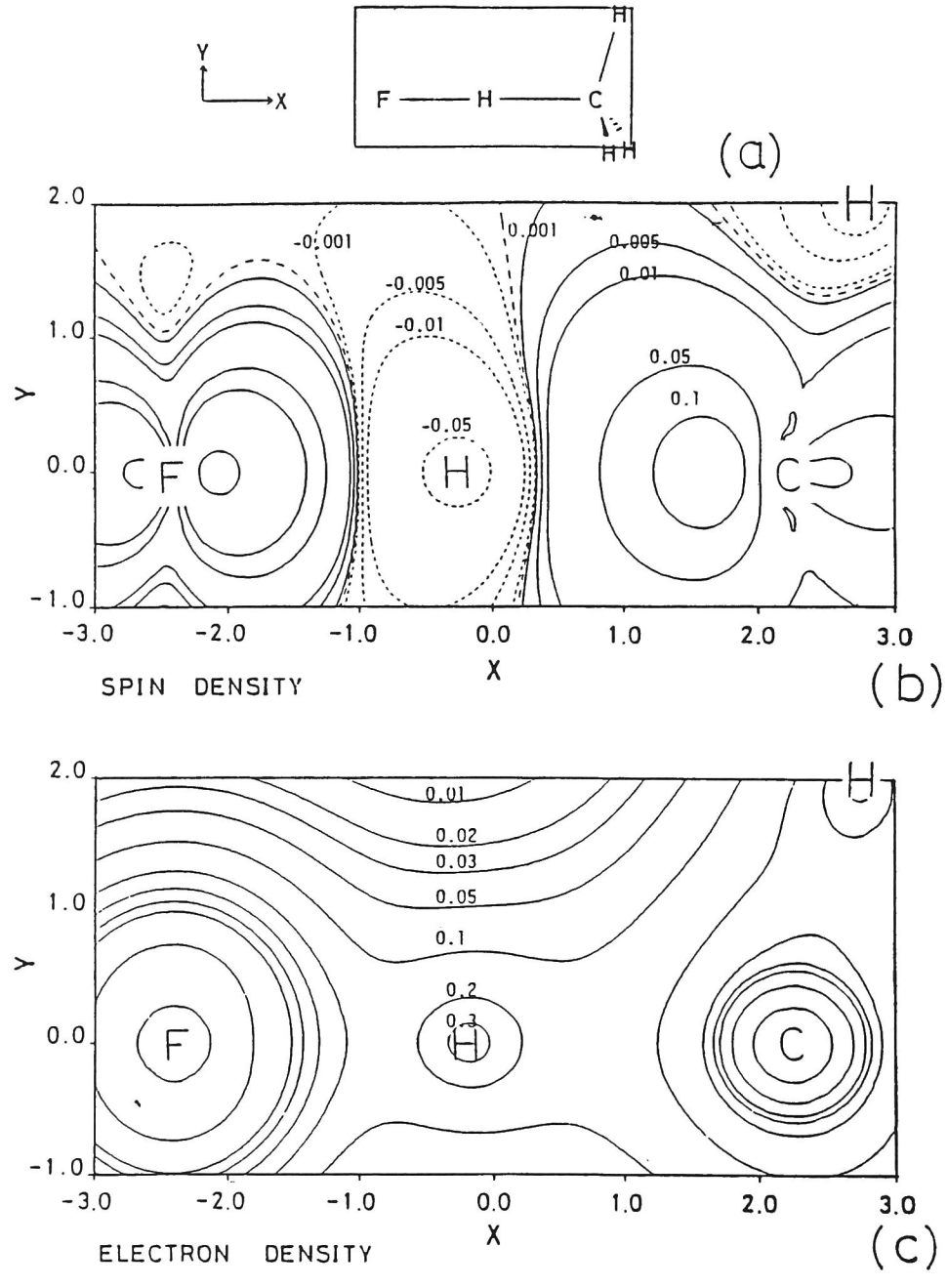

FIG. 5. The contour maps of the adiabatic electron densities at the transition state of the reaction (I): (a) Key of the figures, (b) electron spin density, and (c) electron density. The nuclei in the transition state drawn in the contour maps are located from left to right, at F(− 2.39, 0.00), H(− 0.17, 0.00), C(2.25, 0.00), and H(2.74, 1.97), respectively.

electron density transfer at successive points on the reaction coordinate. In each case, a positive value indicates that the quantity increases during the reaction. In Fig.6(a), a positive(negative) value of spin density change implies the relative increase of the α-spin(β-spin) electron density accompanying the process of the reaction. From the figure, it can be seen that the α-electron density has a greater increase at the H-F bond, and the β-electron density has a greater increase at the C-H bond. Moreover, the region in which the change in β-spin electron density is large, deforms accompanying the motion of the transferred proton. To investigate the electronic process which accompanies the dynamic electron transfer in detail, the dynamic α-spin electron density and the β-spin electron density transfer were calculated, and shown in Figs.6(b), and 6(c), respectively. From Fig.6(b) it can be seen that the α-spin electron is transferred from the bonding region of C-H bond from s=0.0 to s=0.4, on the reaction coordinate, and this is mainly because of the back donation interaction. In particular, the α-spin electron density at the coordinate of -1.9 au increases from s=-0.4 to s=0.0, but decreases at s=0.4 on the reaction coordinate. The magnitude of the changes of α-spin electron density at the coordinate of 1.6 au are not monotonic with respect to the reaction coordinate s. Hence it can be concluded that the transfer of the α-spin electron is almost

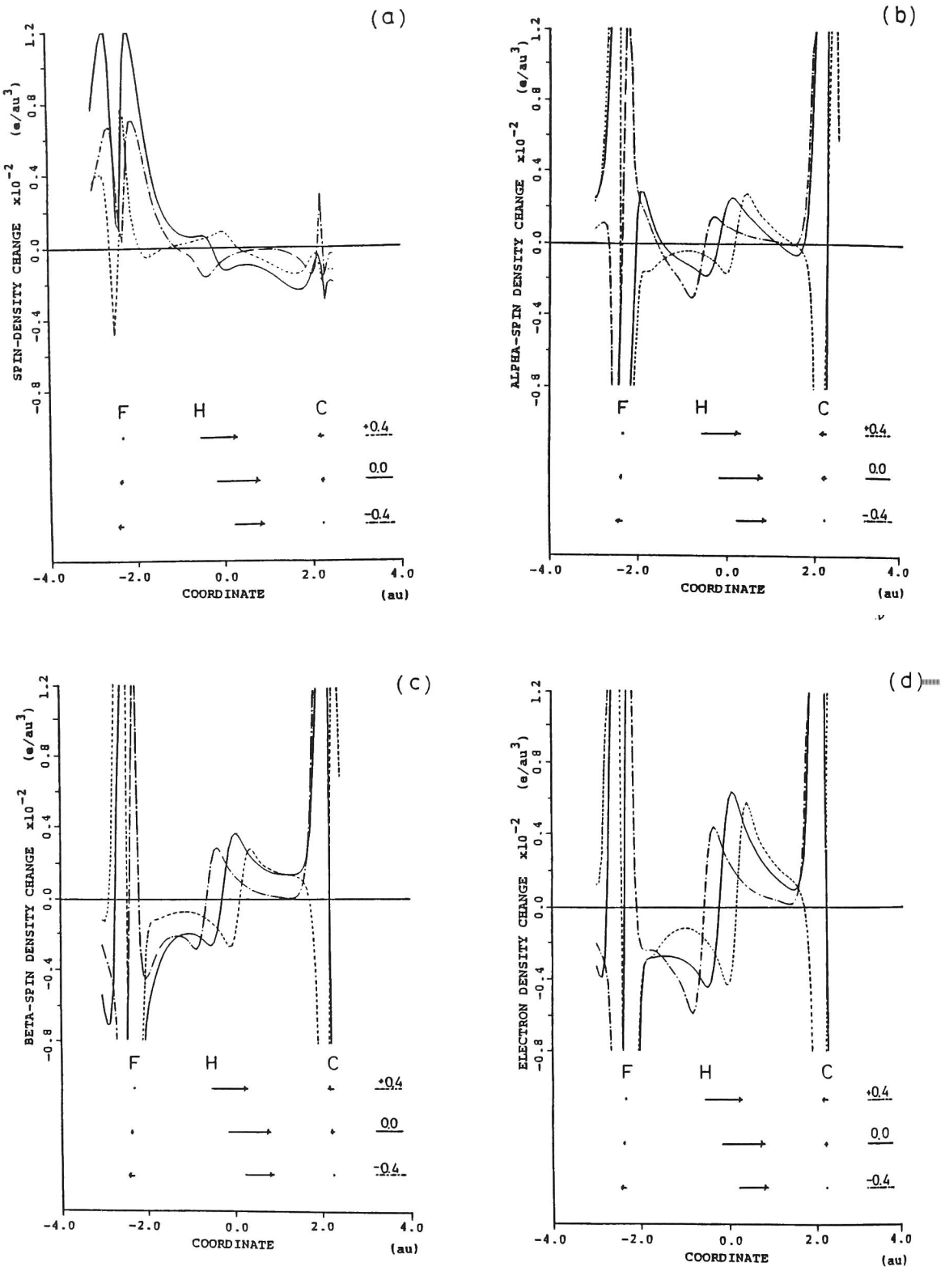

FIG. 6. The dynamic (a) spin transfer, (b) α electron, (c) β electron, and (d) total electron transfer $\langle \rho \rangle_{\text{wave packet}} - \langle \rho \rangle_0$ of the reaction (I) at $s = -0.4, 0.0$, and $+0.4$ on the reaction coordinate. The density changes are calculated on the molecular axis. The location of atoms and the IRC displacement vector are drawn in the figure. We chose $Q_0 = 0.5$.

completed until the molecule attains the transition state, and the transferred proton brings much more α-spin electron density as the reaction proceeds. Fig.6(c) shows that the β-spin electron density is transferred from the neighborhood of the F atom to the C-H bonding region, owing to the donation interaction. Moreover,the β-spin electron is transferred accompanying the proton migration.

The dynamic total electron transfer has been calculated and depicted in Fig.6(d). The heap located around the coordinate of -2.0 which is involved in the H-F bond consists of the total accumulation of the decrease of the β-spin electron density owing to the donation interaction and the increase of the α-spin electron density owing to the back donation interaction. At s=-0.4, the back donation interaction is dominant and the total electron density increases there. But the donation interaction gets more dominant as the reaction proceeds and finally the total electron density decreases at s=0.4.

The importance of the back donation in the early stage of the reaction thus manifested agrees quite well with the discussion of Sec.III.

IV-C. Isomorphic Electron Orbitals

In this section, we discuss the numerical result of the

transformed electron orbitals and their occupation numbers of reaction (I). The adiabatic molecular orbital is obtained as the zero-th order solution of the dynamic Fock equation Eq.(11).[14,15] We use two neighboring points on the intrinsic reaction coordinate s_0 and s_1. The limit as $s_0 \rightarrow s_1$ was obtained numerically when $s_1 - s_0 = \pm 0.001$, and hence we obtained the numerical stabilization.

A pair of transformed electron orbitals at the successive points on the reaction coordinate are largely localized in the atomic region as is shown in Fig.7. The electron orbital 1 is localized largely on the C atom. The electron orbital 2 is localized largely on the F atom. The spatial distribution of the electron orbital 1 and electron orbital 2 at s= -0.4, -0.2, 0.0 are depicted in Figs.8(a), (b), (c), and Figs.9(a), (b), (c), respectively. The electron orbital 1 at each point on the reaction coordinate has a large $2p_Z$ character of the C atom, and the lobe of $2p_Z$ at the inside of the supermolecule is extended over the other side. Especially, the electron orbital 1 at s= -0.4 has the lobe of the $2p_Z$ orbital of the C atom that stays beyond the F atom. Hence, the electron orbital 1 at each point on the reaction coordinate is localized strongly to the $2p_Z$ orbital of the C atom, though there is some contamination of the 2s or $2p_Z$ orbital of the F atom. The electron orbital 2 at each point on the reaction coordinate has a large $2p_Z$ character of the F atom, and the lobe of the

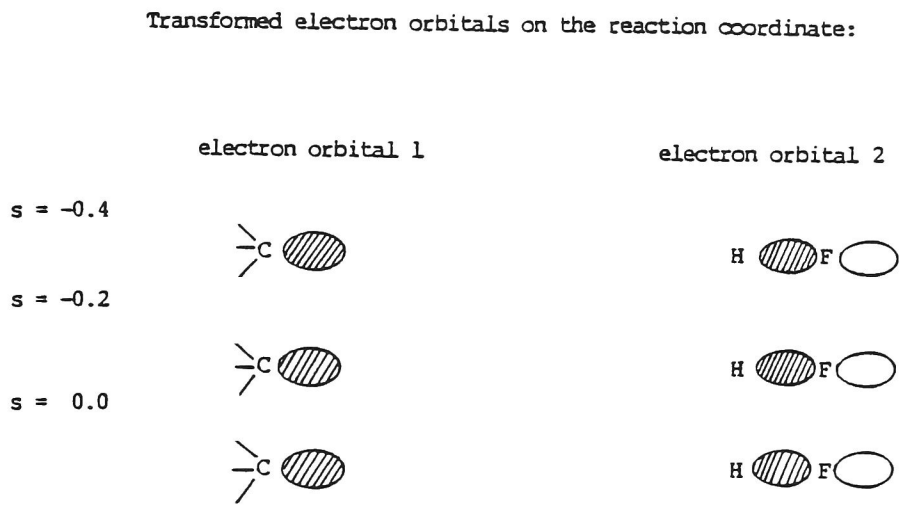

FIG. 7. Schematic representation of the transformed electron orbitals which are localized on the C atom or the F atom at $s = -0.4$, -0.2, and 0.0 on the reaction coordinate.

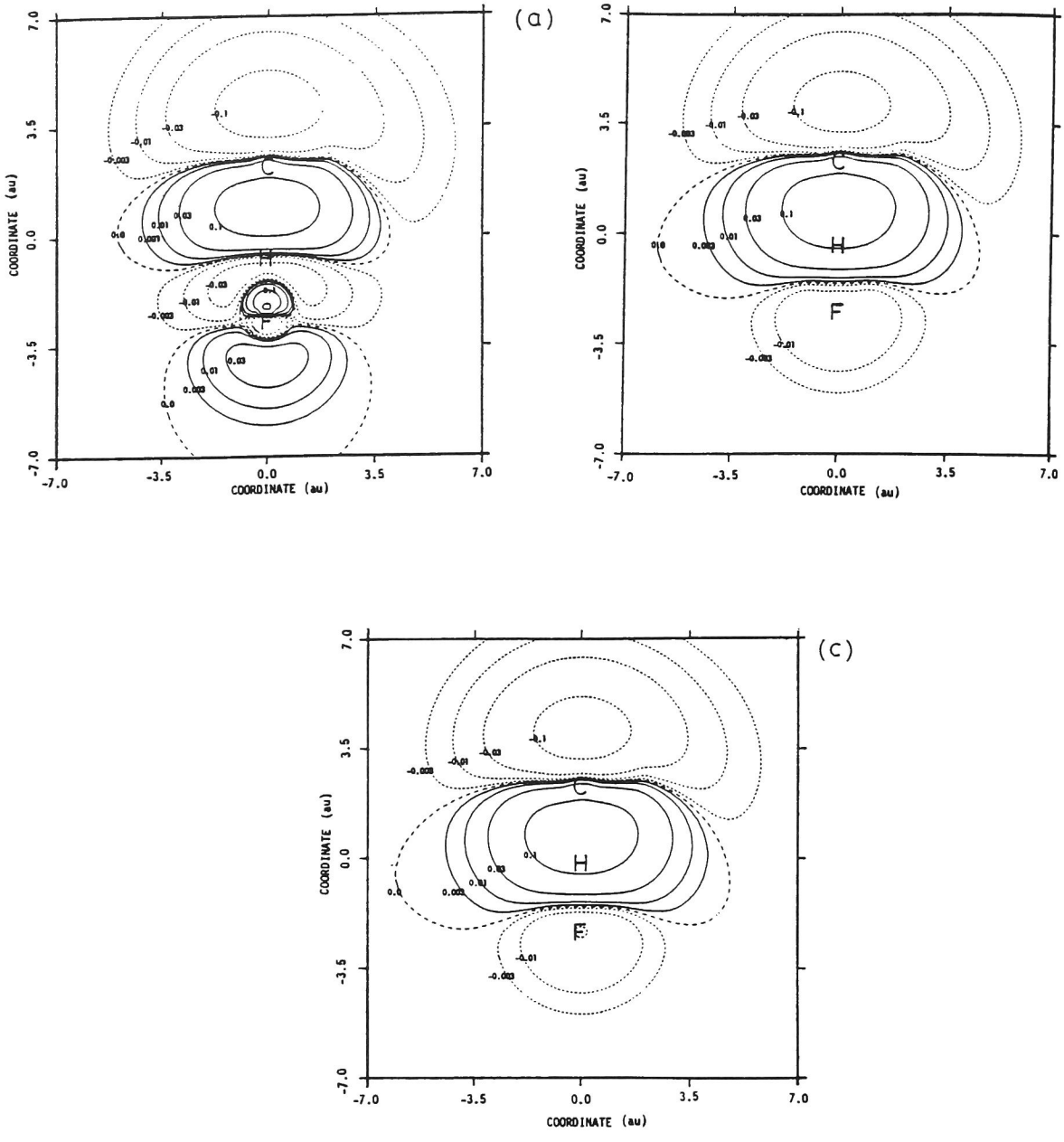

FIG. 8. Spatial distribution of the transformed electron orbital 1 which is localized on the C atom at (a) $s = -0.4$, (b) $s = -0.2$, and (c) $s = 0.0$ on the reaction coordinate.

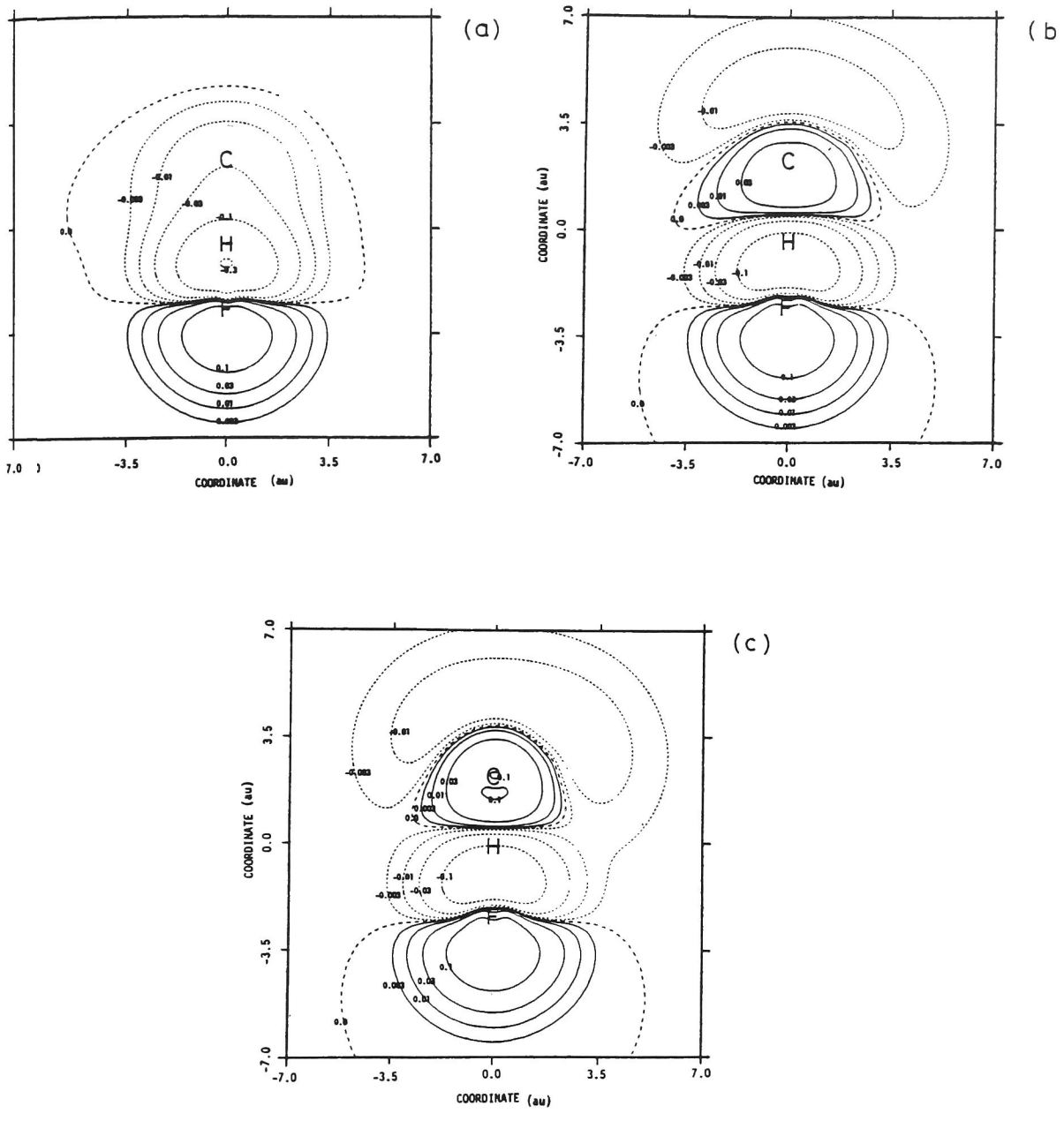

FIG. 9. Spatial distribution of the transformed electron orbital 2 which is localized on the F atom at (a) $s = -0.4$ (b) $s = -0.2$, and (c) $s = 0.0$ on the reaction coordinate.

$2p_z$ orbital at the inside of the supermolecule is extended over the other side. Especially at s= -0.2 and s=0.0 the electron orbital 2 has the lobe of the $2p_z$ orbital of the F atom that stays beyond the C atom. Thus the electron orbital 2 at each point on the reaction coordinate is localized strongly to the $2p_z$ orbital of the F atom, though there is some contamination of the 2s orbital of the C atom at s= -0.2 and s= 0.0, respectively. In either case, the transformation induces localization of the electron orbital, though the transformation operator itself does not contain any localization terms, such as self energy integral of electron.[30-31]

The change of the occupation numbers of the transformed electron orbitals along the reaction coordinate is tabulated in Table 2. It should be noted that the α-electron occupation number of the electron orbital 1 does not largely change, and the β-electron occupation number increases strongly accompanying the reaction process. On the other side, the α-electron occupation number of the electron orbital 2 does not change largely, and the β-electron occupation number decreases accompanying the reaction process. In other words, the β-electron transfers from the electron orbital 2 which is strongly localized to the $2p_z$ orbital of the F atom to the electron orbital 1 which is largely localized to the $2p_z$ orbital of the C atom. It can be seen that this change of the

TABLE II. Change of occupation number of electron orbitals along the reaction coordinate.

s[a]	−0.4	−0.2	0.0
$\bar{\nu}_1^{\alpha}$ [b]	0.677	0.766	0.629
$\bar{\nu}_1^{\beta}$ [c]	0.054	0.258	0.402
$\bar{\nu}_2^{\alpha}$ [b]	0.782	0.698	0.771
$\bar{\nu}_2^{\beta}$ [c]	0.805	0.578	0.454

[a] Intrinsic reaction coordinate, the unit and the location are the same with Fig. 2(a).
[b] α electron occupation number of Eq. (9).
[c] β electron occupation number of Eq. (9).

occupation number of the special electron characterizes the initial reaction process. This agrees well with the previous result that the back donation is larger than the donation at the early stage of the reaction. Moreover the β-electron occupation number of the electron orbital 1 changes largely at s= -0.2, and this also agrees well with the result that the spin polarization within the HF fragment increases largely from s= -0.4 to s= -0.2.

Thus we can demonstrate the electronic process accompanying the chemical reaction, in terms of the concept of the change of the occupation numbers of the electron orbitals which are determined uniquely all over the reaction process and almost fixed in certain configurations.

V. CONCLUDING REMARKS

We have developed the analysis of the dynamic electron transfer accompanying the chemical reaction process, by introducing the new criterion of an isomorphism of the electron orbital manifolds at the distinct points of the reaction coordinate. Then, we can describe the electronic process of the chemical reaction as the transition process of the occupation number within electron orbital manifolds which are constructed to have isomorphic equivalency during the reaction process.

According to the new criterion, the spatial distribution of the electron orbital is largely affected and the orbital is localized strongly, though the transformation operator itself does not contain any explicit localization terms such as self energy integrals. The dynamic electron transfer accompanying the chemical reaction process can be analyzed in terms of the orbital contribution by using transformed electron orbitals. The application of this method of analysis to the reaction (I) gives good agreement with the usual analysis of canonical electron orbitals, and gives more detailed and direct information of the electron transition process on the reaction coordinate. The donation and back donation interaction or the charge transfer and back charge transfer interaction between the two fragments are elucidated by the change of the occupation number along the reaction coordinate.

The analysis of dynamic electron transfer and the new transformation operator presented in this chapter proves to be useful for the study of the electronic process accompanying the reaction (I). The analysis will be useful also in the study of the electron transfer reaction in biological systems where the electronic process influenced by the molecular vibration itself is an interesting problem in the field of chemical physics.

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Chapter 3

Electron Transport Accompanying Molecular Vibration

I. INTRODUCTION

The development of a molecular device based on a synthetic metal involves two important problems. First, the synthesis of high conduction polymers in itself, and second, the doping which assists the inter-chain electron transfer between the polymer chains. Because the molecular device no longer has the translational symmetry in the large, the microscopic vibronic interaction should play an important role in the electron transport property, as is the case with amorphous semiconductors. It will then be interesting to investigate the electron density fluctuation accompanying molecular vibration[1-3]. A more detailed analysis of the electron rearrangement accompanying molecular vibration uses the change of the occupation numbers of the electron orbitals which are defined so as to follow the smooth electron current accompanying molecular vibration[4].

II. THEORY

The density change accompanying molecular vibration is

described by the dynamic electron density $\langle\rho\rangle_n$ [1-3];

$$\langle\rho\rangle_n \equiv \int \rho(Q)\Psi_n(Q)^*\Psi_n(Q)dQ, \tag{1}$$

where Q, ρ, and Ψ_n denote the normal coordinate of molecular vibration, the electron density, and the wavefunction of the n-th excited vibrational state, respectively. The dynamic electron density has an interesting additive property: when the molecule is vibrationally excited from the n-th to the n+1-th excited state, the increment of the electron density is independent of n. Time-dependent dynamic electron density can also be described by substituting the wavepacket wavefunction.

To investigate a large amplitude molecular vibration, we shall use the Intrinsic Reaction Coordinate(IRC) concept of Fukui[5]. IRC is defined as the steepest descent path of an adiabatic potential. It has been shown, by applying the differential geometry method, that IRC converges most probably to the weakest normal mode of molecular vibration at an equilibrium point of the adiabatic potential[6]. Then it can be said that IRC is an extension of the normal coordinate to large amplitude molecular vibration.

Electron orbitals at two points s_0 and s_1 of IRC $\{\psi_i(0)\}$ and $\{\psi_j(1)\}$, are transformed so as to make their overlap matrix $||S_{ij}||$ diagonal[4]. Then, the isomorphic equivalency is brought about as shown in Fig. 1. If we take the limit of $s_1 \rightarrow s_0$, and after that let s_0 be varied as we move along IRC, then we obtain the electron orbitals which

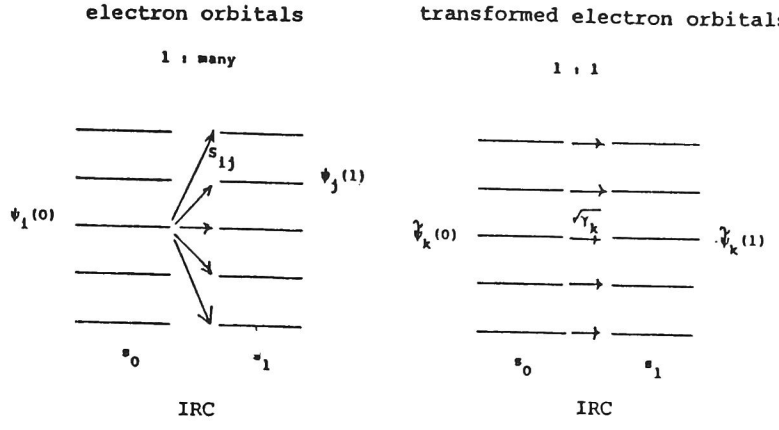

Fig. 1. One-to-one correspondence in the electron orbital manifolds at two points of the IRC.

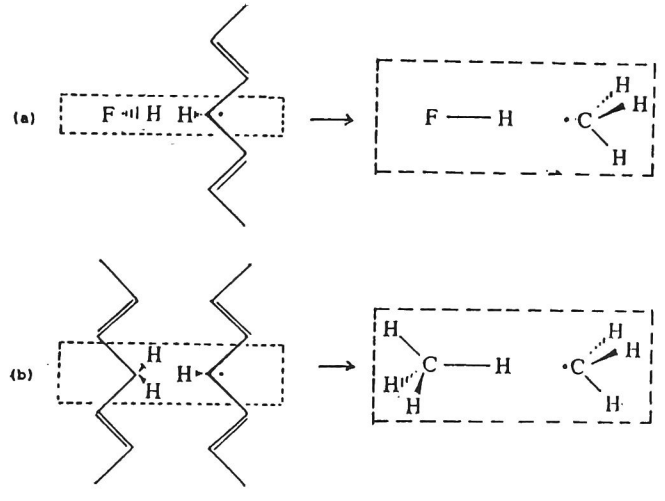

Fig. 2. Local site models of electron transfer induced by molecular vibration. Between neutral soliton of PA and (a) HF molecule (b) local defect of PA.

represent a smooth electron current accompanying molecular vibration. We define the occupation number $\tilde{\nu}_k$ and the orbital energy $\tilde{\varepsilon}_k$ of the transformed orbitals $\{\tilde{\psi}_k\}$ as follows:

$$\tilde{\nu}_k \equiv \langle \tilde{\psi}_k \mid \rho \mid \tilde{\psi}_k \rangle , \tag{2}$$

$$\tilde{\varepsilon}_k \equiv \langle \tilde{\psi}_k \mid F \mid \tilde{\psi}_k \rangle \tag{3}$$

where F denotes the Fock operator of the electrons. The smooth electron current accompanying molecular vibration is represented by the correlation diagram between the orbital energy and the occupation number. A discrete change of occupation number can be induced by the molecular vibration; this may be a measure of the temperature of the vibronic states which is different from that of Boltzmann and Fermi-Dirac statistics. All the numerical calculations are performed at the UHF[7], 4-31G[8] level. The Gaussian80 program[9] with the requisite new subroutines was used for this study.

III. RESULTS

The local site model used are schematically shown in Fig. 2. Two chemical reaction systems are used:

$$CH_3 + HF \rightarrow CH_4 + F , \tag{I}$$

$$CH_3 + CH_4 \rightarrow CH_4 + CH_3 , \tag{II}$$

as models of the electron transfer between neutral soliton of PA and (I) dopant HF molecule, and (II) defect in another PA, respectively.

The dynamic α-electron and β-electron transfer characteristic of the chemical reaction (I) at the transition state are shown in Fig. 3. The minimum uncertainty wavepacket is used as a first approximation to include the quantum effect of the large amplitude molecular vibration along the IRC. Then the electron current is estimated by;

$$\langle\rho\rangle_0-\rho(0)\sim\{1/(4\omega)\}\,(\partial^2/\partial Q^2)\rho(0), \tag{4}$$

which is the difference of the 0-point dynamic electron density and the electron density in the clamped nuclei limit. This term represents how the 0-point vibrational motion affects the electron density distribution. Fig. 3 shows that the β-electron density around F atoms decreases greatly, and the α-electron change is small. The quantum effect of the vibrational motion induces the electron current toward the positive direction of the reaction (I), which is mainly due to the β-electron current. As a result, it acts to destroy the neutral soliton of PA. On the other hand, a vibrational mode orthogonal to IRC at the transition state induces the opposite dynamic β-electron transfer as shown in Fig. 4. The quantity estimated is given by;

$$\langle\rho\rangle_n-\langle\rho\rangle_0\sim\{n/(2\omega)\}\,(\partial^2/\partial Q^2)\rho(0), \tag{5}$$

which represents the density change accompanying the vibrational excitation from the 0-point state to the n-th excited state. The vibrational quantum numbers are depicted in the figure. The density change is small compared to those

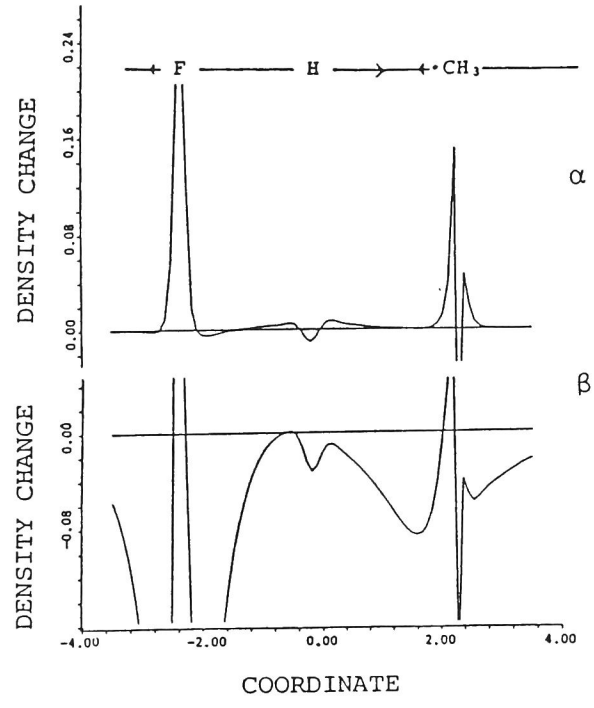

Fig. 3. Dynamic α-, and β-electron transfers along the IRC of reaction (I) on the molecular axis.

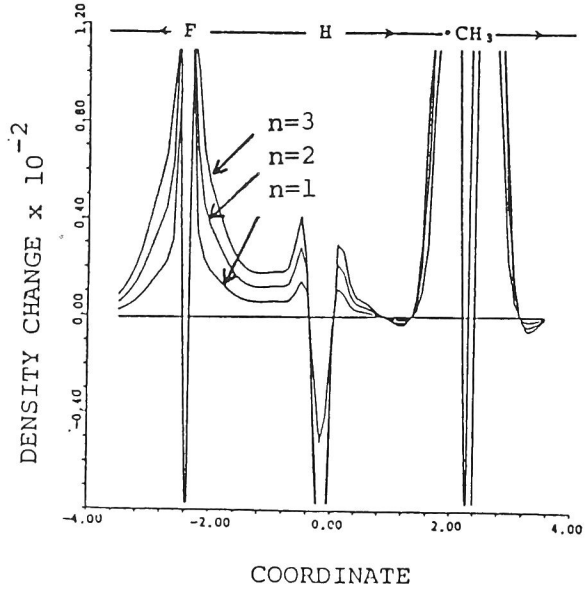

Fig. 4. Dynamic β-electron transfer accompanying the vibration orthogonal to the IRC of reaction (I).

accompanying vibrational motion along IRC. It is approximately 1/20 of that. But, Fig. 4 shows that the β-electron density is accumulated in the HF bond region to disturb the bond dissociation of the HF fragment. As a result, it can be concluded that this vibrational motion orthogonal to the IRC induces the inverse electron current of the reaction (I), though the magnitude of the electron current is small. It hardly affects the passage of the neutral soliton.

Dynamic α-electron and β-electron transfers along IRC of reaction (II) at the transition state are shown in Fig. 5. The electron current is completely symmetric, which is due to the symmetry of the transition state. Again, the β-electron transfer is dominant. A more detailed analysis of the electron transport accompanying molecular vibration is performed in terms of the transformed electron orbitals for the reaction (I). For the β-electron transport along IRC, the orbital energy-occupation number correlation diagram is obtained and shown in Fig. 6. The two electron orbitals change their orbital energies and occupation numbers drastically. Fig. 6 shows that a β-electron is transferred from the $\tilde{\psi}_2$ orbital, which is localized strongly on the 2p orbital of the F atom, to the $\tilde{\psi}_1$ orbital, which is localized strongly on the 2p orbital of the C atom[4]. As a result, it is concluded that the large amplitude vibrational motion along IRC will heat a special electron which stays at a distinct point of the

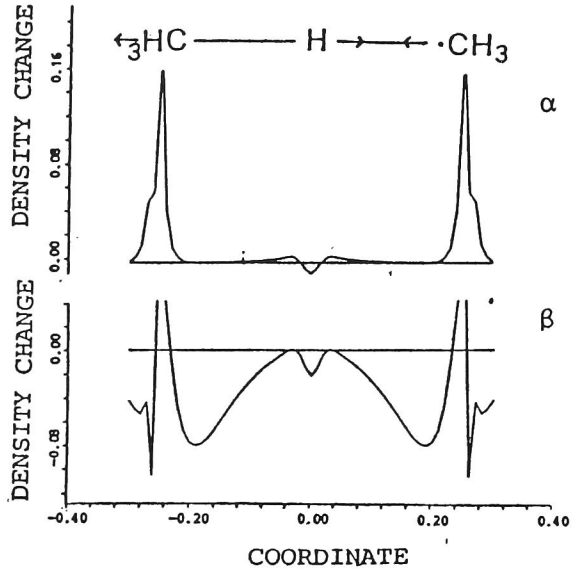

Fig. 5. Dynamic α-, and β-electron transfers along the IRC of reaction (II) on the molecular axis.

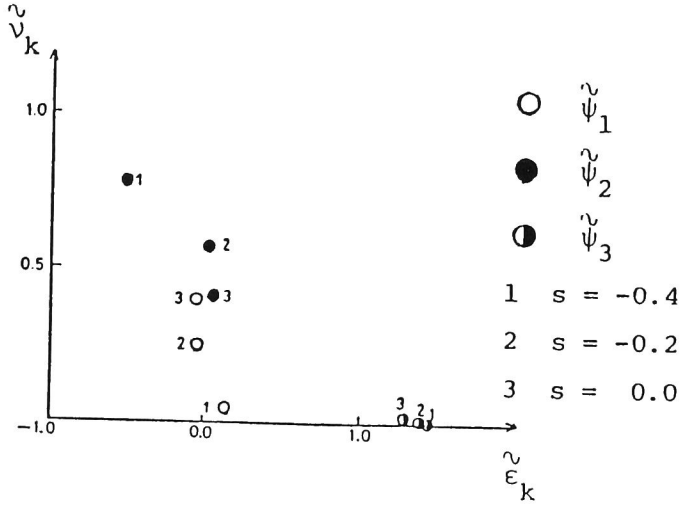

Fig. 6. The change of β-electron orbital energy-occupation number correlation along the IRC of reaction (I). The transition state is located at the origin of the IRC: s=0.0, and the IRC is negative on the reactant side.

correlation diagram. This conclusion is reasonable also in the light of the frontier electron theory.

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Chapter 4

The Electronic Flexibility of the Cyclopropenyl Radical Against the Molecular Vibration

I. INTRODUCTION

Recently, Carter has suggested the intrinsic importance of molecular tips in future electronic devices.[1] Since then, many models have been proposed as candidates for molecular devices. The theoretical understanding of the response properties of the electronic structure of a molecule to internal and external perturbations; e.g. molecular vibration and electric and/or magnetic fields, have become more important from this point of view.[2] Especially, the microscopic vibronic interaction should play an important role in the electric conductivity of molecular aggregates, as the molecular device no longer has any translational symmetry.[3] It is then interesting to investigate how the electronic structure is affected by the molecular vibration, on the basis of the molecular orbital method.[4] We have previously proposed to generalize the Amos-Hall corresponding orbital method[5] to introduce a smooth connection of the electron orbital manifolds accompanying the motion on the base space reaction coordinate.[6] The electron transport accompanying a molecular vibration is then expressed by the occupation number change of

the electron orbital obtained from the rearrangement operator, as discussed in this part.[6,7] Thus we have made it possible to formulate the operator, which is like an evolution operator[8] for the electron orbital whose perturbation is induced by the time-dependent molecular vibration without being affected by the nonorthogonality of the perturbed wavefunction up to the second order. The rearrangement operator of the generalized corresponding orbitals which we named the isomorphic electron orbitals has a relation with the nonadiabatic coupling operator of the dynamic Fock equation,[9] which satisfies the exact variational condition.

In this chapter, we will analyze the vibrationally induced electron transport of the cyclopropenyl radical which may be used as a unit in the tetracyclic soliton valve which is suggested by Carter as the switching tip of the molecular device.[10] The facility or difficulty of the electron transport accompanying the molecular vibration is examined in detail by utilizing the isomorphic electron orbitals. This will have a theoretical connection with the Kohn anomaly in the field of condensed matter physics.[11]

II. THE DERIVATIVE EXPRESSION OF THE REARRANGEMENT OPERATOR OF THE ISOMORPHIC ELECTRON ORBITALS

We have introduced the isomorphic electron orbitals in

the previous chapters.[6,7] Now we will review the isomorphic electron orbitals and present a derivative expression for the rearrangement operator of the orbital, then we will discuss the relation between this operator and the dynamic Fock operator.[9] The quantum mechanical treatment of the nuclear motions in the rearrangement operator is discussed in Sec.IIB.

A. Classical treatment.

The natural orbitals[12] $\psi_m(0)$ and $\psi_j(1)$ at two distinct points s_0 and s_1 of the reaction coordinate[13,14] have overlap integrals S_{mj};

$$S_{mj}=\langle \psi_m(0) | \psi_j(1) \rangle \quad . \tag{1}$$

S_{mj} is not diagonal in general, and hence there is no one-to-one correspondence in the electron orbital manifolds at s_0 and s_1 in the criterion of the overlap integrals S_{mj}. The rearrangement operator $||R_{ij}||$ is defined as follows;

$$R_{ij} = \sum_m S_{mi}^* S_{mj} \quad , \tag{2.a}$$

$$R_{ij} = R_{ji}^* \quad , \tag{2.b}$$

the eigenvalues and eigenvectors of the operator are denoted by γ_k and U_{ik} , respectively and each eigenvector is normalized;

$$\sum_j R_{ij} U_{jk} = U_{ik}\gamma_k \quad , \tag{3.a}$$

$$\sum_i U_{ik}^* U_{in} = \delta_{kn} \ . \tag{3.b}$$

The transformed electron orbitals $\tilde{\psi}_k(0)$ and $\tilde{\psi}_k(1)$ are obtained by using U_{jk}, S_{mj} and γ_k;

$$\tilde{\psi}_k(1) = \sum_i U_{ik}\psi_i(1) \ , \tag{4.a}$$

$$\tilde{\psi}_k(0) = (1/\sqrt{\gamma_k})\sum_j\sum_m S_{mj}U_{jk}\psi_m(0) \ . \tag{4.b}$$

The overlap matrix of the two sets of transformed orbitals $\{\tilde{\psi}_k(1)\}$ and $\{\tilde{\psi}_k(0)\}$ is diagonal, so that the following orthonormality relations are obtained;

$$\langle \tilde{\psi}_k(0) | \tilde{\psi}_n(0) \rangle = \delta_{kn} \ , \tag{5.a}$$

$$\langle \tilde{\psi}_k(1) | \tilde{\psi}_n(1) \rangle = \delta_{kn} \ , \tag{5.b}$$

$$\langle \tilde{\psi}_k(0) | \tilde{\psi}_n(1) \rangle = \sqrt{\gamma_k}\,\delta_{kn} \ . \tag{5.c}$$

If we take the limit s_1 -> s_0 then $\{\tilde{\psi}_k(1)\}$ -> $\{\tilde{\psi}_k(0)\}$ and after that let s_0 be varied as we move along the reaction coordinate, we can get a set of electron orbitals $\{\tilde{\psi}_k\}$ which describe the smooth electron current accompanying a chemical reaction. The occupation numbers $\{\tilde{\nu}_k\}$ of the electron orbitals $\{\tilde{\psi}_k\}$ are defined[6,7] as the expectation values of a diagonal element of the first order density matrix ρ[12] by using the basis electron orbitals $\{\tilde{\psi}_k\}$;

$$\tilde{\nu}_k = \langle \tilde{\psi}_k | \rho | \tilde{\psi}_k \rangle \ , \tag{6.a}$$

$$\rho = \sum_i \nu_i \psi_i^* \psi_i , \tag{6.b}$$

where ν_i is a occupation number[12] of the natural orbital ψ_i. In the Eq.(6), $\tilde{\psi}_k(0)$ and $\tilde{\psi}_k(1)$ are united in a single symbol $\tilde{\psi}_k$, because of the limit property. Similarly the orbital energies $\{\tilde{\varepsilon}_k\}$ of the electron orbitals $\{\tilde{\psi}_k\}$ are defined[7] as the expectation values of a natural orbital Hamiltonian operator[14], or Fock operator F, by using the basis electron orbitals $\{\tilde{\psi}_k\}$;

$$\tilde{\varepsilon}_k = \langle \tilde{\psi}_k | F | \tilde{\psi}_k \rangle . \tag{7}$$

The change in the correlation diagram of $\{\tilde{\varepsilon}_k\}$ and $\{\tilde{\nu}_k\}$ accompanying the chemical reaction was examined within the Hartree-Fock approximation, and it was concluded that there were two characteristic isomorphic electron orbitals which represented a smooth electron transport of the system examined.[7]

It is interesting to present a derivative expression of the rearrangement operator, because it enables us to discuss the analytical structure of the rearrangement operator. A Taylor series expansion of R_{ij} by $\Delta s = s_1 - s_0$ up to second order is given as follows;

$$R_{ij} = R_{ij}^{(0)} + R_{ij}^{(1)} \Delta s + R_{ij}^{(2)} \Delta s^2 + o(\Delta s^3) , \tag{8.a}$$

$$R_{ij}^{(0)} = \delta_{ij} , \tag{8.b}$$

$$R_{ij}^{(1)} = 0 , \tag{8.c}$$

$$R_{ij}^{(2)} = - \langle \partial \psi_i / \partial s | \partial \psi_j / \partial s \rangle$$

$$+\sum_{m}\langle \partial\psi_i/\partial s \,|\, \psi_m\rangle\langle \psi_m \,|\, \partial\psi_j/\partial s\rangle . \qquad (8.d)$$

If we substitute Eq.(8) into Eq.(3.a), we have;

$$\sum_{j}(\delta_{ij}+R_{ij}^{(2)}\Delta s^2)U_{jk}=U_{ik}\gamma_k . \qquad (9)$$

Then if R_{ij} converges up to second order in the expansion of Eq.(8.a), the two rearrangement operators are completely equivalent, because $R_{ij}^{(2)}$ which satisfies the following relationship;

$$\sum_{j}R_{ij}^{(2)}U_{jk}=U_{ik}\gamma_k^{(2)} , \qquad (10)$$

will satisfy Eq.(9) and hence Eq.(3). It should be noted that, in that case, γ_k is given as follows;

$$\gamma_k=1+\gamma_k^{(2)}\Delta s^2 . \qquad (11)$$

If we use the molecular orbitals $\{\psi_j\}$ which satisfy the following orthonormal condition;[9]

$$\langle \Psi_{nuc} \,|\, \langle \psi_i \,|\, \psi_j\rangle \,|\, \Psi_{nuc}\rangle=\delta_{ij} , \qquad (12)$$

to construct the single Slater determinantal electronic wavefunction Ψ_{elec}, where Ψ_{nuc} denotes the nuclear wavefunction, then the total energy of the closed shell molecular system $E=\langle \Psi | H | \Psi\rangle$, where H denotes the molecular Hamiltonian and Ψ denotes the molecular wavefunction given by;

$$\Psi=\Psi_{elec}\Psi_{nuc} , \qquad (13)$$

can be expressed as follows;

$$E=\langle \Psi_{nuc} \,|\, 2\sum_{i}^{occ}H_i+\sum_{ij}^{occ}(2J_{ij}-K_{ij}) \,|\, \Psi_{nuc}\rangle$$

$$+\langle \Psi_{nuc} | \hat{T}_n + \hat{V}_{nn} | \Psi_{nuc} \rangle + \langle \Psi_{nuc} | D | \Psi_{nuc} \rangle , \quad (14)$$

where H_i, J_{ij}, and K_{ij} denote the one electron integral, Coulomb, and exchange integral matrix of the usual Hartree-Fock electronic energy expression, and $\hat{T}_n$, $\hat{V}_{nn}$ denote the kinetic energy operator of nuclei and nuclear-nuclear Coulomb interaction operator, respectively. The concrete form of the nonadibatic coupling energy term D is given as follows;

$$D=\sum_{ij}^{occ} (\langle \partial\psi_j/\partial Q | \partial\psi_j/\partial Q \rangle \delta_{ij}$$

$$-\langle \partial\psi_j/\partial Q | \psi_i \rangle \langle \psi_i | \partial\psi_j/\partial Q \rangle) , \quad (15)$$

where Q denotes the normal coordinate of molecular vibration and occ denotes that the summation is performed over the occupied molecular orbitals. If we substitute the canonical solution of the dynamic Fock equation in the clamped nuclei limit $\{\psi_i\}$, which extremize the total energy of the molecule into Eq.(8.d), D can also be expressed as follows;

$$D=-\sum_{i}^{occ} R_{ii}^{(2)} , \quad (16)$$

where the summation over m in Eq.(8.d) is limited to the occupied orbitals. It should be noted that the reaction coordinate is identified with the normal coordinate because they coincide locally at the stable point.[14] If we use the canonical "solution" $\{\psi_j\}$ of the equation;

$$\Delta\psi_i=\varepsilon_i\psi_i , \quad (17)$$

where Δ is a nonadibatic coupling operator of the dynamic Fock

equation[9] in the clamped nuclei limit to construct $R_{ij}^{(2)}$ in Eq.(8.d), following relation can be obtained;

$$R_{ij}^{(2)} = -\langle \psi_i | \Delta | \psi_i \rangle - (1/2)\langle \partial\psi_i/\partial s | \partial\psi_j/\partial s \rangle , \qquad (18)$$

again, the summation over m in Eq.(8.d) is limited to the occupied orbitals. These are the relations between the dynamic Fock equation and the derivative expression of the rearrangement operator $R_{ij}^{(2)}$. $R_{ij}^{(2)}$ has relations to the nonadiabatic coupling energy and the nonadiabatic coupling operator through Eq.(16) and Eq.(18).

B. Quantum mechanical treatment.

In the classical treatment of Sec.IIA, the electron rearrangement at the distance Δs is estimated by the power series of Δs . If we consider quantum mechanical vibration, then each order of the nuclear fluctuation is estimated by a non-null finite value. The general expression of the rearrangement operator may then be defined as follows.

$$\overline{R}_{ij} = \langle R_{ij} \rangle_{av.} , \qquad (19)$$

where $\langle \rangle_{av.}$ denote the statistical average with respect to the quantum mechanical nuclear vibration. Of course, the nuclear vibration is not limited to the direction of the reaction coordinate, and hence, the fluctuation is not limited to the point on the reaction coordinate. This rearrangement operator is Hermitian and has the eigenvalue and eigenvector as

follows;

$$\sum_j \overline{R}_{ij}\overline{U}_{jk} = \overline{U}_{ik}\overline{\gamma}_k \ , \tag{20.a}$$

$$\sum_i \overline{U}_{ik}^{*}\overline{U}_{in} = \delta_{kn} , \tag{20.b}$$

which are the counterparts of Eqs. (3.a) and (3.b). The transformed electron orbitals are given as follows;

$$\overline{\psi}_k(1) = \sum_i \overline{U}_{ik}\psi_i(1) \ , \tag{21.a}$$

$$\overline{\psi}_k(0) = (1/\sqrt{\overline{\gamma}_k})\sum_j\sum_m S_{mj}\overline{U}_{jk}\psi_m(0) \ , \tag{21.b}$$

which are the counterparts of Eqs.(4.a) and (4.b). Finally we obtain the orthonormal relations;

$$\langle\langle \overline{\psi}_k(0) | \overline{\psi}_n(0)\rangle\rangle = \delta_{kn} \ , \tag{22.a}$$

$$\langle\langle \overline{\psi}_k(1) | \overline{\psi}_n(1)\rangle\rangle = \delta_{kn} \ , \tag{22.b}$$

$$\langle\langle \overline{\psi}_k(0) | \overline{\psi}_n(1)\rangle\rangle = \sqrt{\overline{\gamma}_k}\,\delta_{kn} \ , \tag{22.c}$$

which are the counterparts of Eqs.(5.a)-(5.c). It should be noted again that the $\overline{\psi}_n(1)$ denotes the n-th orbital at a point, say P_1, in the neighborhood of s_0, which is not limited at s_1. Let s_0 be varied as we move along the reaction coordinate, then we get the electron orbitals $\{\overline{\psi}_k\}$ which represent the smooth electron current accompanying the local quantum fluctuation of the molecular vibration. The occupation number and the orbital energy may also be defined as follows;

$$\overline{\nu}_k = \langle \overline{\psi}_k | \rho | \overline{\psi}_k \rangle \ , \tag{23}$$

$$\tilde{\varepsilon}_k = \langle \bar{\psi}_k | F | \bar{\psi}_k \rangle , \tag{24}$$

which are the counterparts of Eqs.(6.a) and (7), respectively. It should be noted that if we consider only the zero-point vibrations at a stable equilibrium point, then the leading term of $\bar{R}_{ij}$ in Eq.(12) is given by the contribution of the motion along the IRC;

$$\bar{R}_{ij} \sim R_{ij}^{(0)} + \{1/(2\omega_{min})\} R_{ij}^{(2)} , \tag{25}$$

where ω_{min} denotes the minimum vibrational frequency of the system at the stable equilibrium point, and where we have used the result that the IRC converges to the normal mode with the minimum force constant by virtue of the stable limit theorem.[14(b)] This shows that the electron rearrangement along the IRC plays a leading role at the absolute zero temperature in the quantum mechanical treatment.

III. THE ELECTRONIC FLEXIBILITY OF THE ISOMERIZATION CHANNEL OF THE CYCLOPROPENYL RADICAL VALVE UNIT

Fig.1 shows the soliton valve which Carter has suggested as a molecular switching device.[10] The soliton valve contains a cyclopropenyl radical fragment as a valve unit. The soliton passage is mediated through the dimerized ethylenic or allylic structure of cyclopropenyl radical. The actual action of the valve is not so easy as might be anticipated from Fig.1, because there is another reaction channel in the 3D and 6B

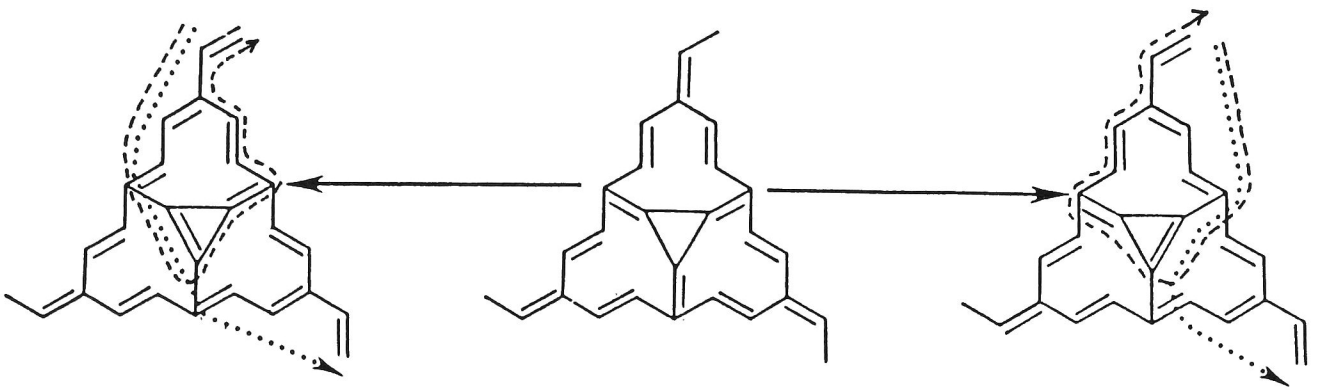

Fig. 1 The plausible operations of the soliton valve. The soliton passage channel is depicted by the dotted line, and the reflection channel is depicted by the broken line. The flexibility of the electronic structure of cyclopropenyl radical against the molecular vibration may have a relation with the operations.

states of the valve for the soliton passage channel (depicted by the dotted line in Fig.1) and the total reflection channel (depicted by the broken line in Fig.1), i.e. an isomeric reaction channel between the ethylenic and allylic structure of the cyclopropenyl radical valve unit. The existence of the isomerization channel was demonstrated by an ESR experiment.[16] We will discuss the electronic flexibility of the isomerization reaction channel of the cyclopropenyl radical to clarify this problem.

A. THE ISOMERIZATION REACTION COORDINATE OF THE POTENTIAL ENERGY SURFACE OF THE CYCLOPROPENYL RADICAL

An equilateral cyclopropenyl radical is unstable because the odd electron must occupy one of the degenerate electron orbitals.[17] The cyclopropenyl radical then distorts to have six local minimum structures, which can be grouped into the two structures, i.e. ethylenic and allylic. The local minima of the potential energy surface of the cyclopropenyl radical were located at the Hartree-Fock level.[18] The reaction coordinate region of the potential energy surface is still unknown. Even if one could locate the saddle point of the potential energy surface, the reaction coordinate would be very complicated and then the electronic process along the reaction coordinate would also be complicated, since the local

minima do not have planar structures.[18] Furthermore the potential energy surface may be very sensitive to electronic correlation. To avoid numerical ambiguities we shall adopt the pseudo rotation coordinate,[17,19] instead of the steepest descent reaction coordinate,[13] which is much affected by the accuracy of the potential energy surface. And we shall use the UHF[20] 4-31G[21] electronic wavefunction. The quality of the wavefunction is good enough to discuss the response property of the electrons to the molecular vibration, which is the object of our interest, because the response property is so universal as to allow one to neglect electron-electron interactions, for example in the theory of the Kohn anomaly and related subjects.[11] The Gaussian80[22] and Gaussian82[23] programs and requisite subroutines are used in this study.

The stationary structures both ethylenic and allylic of the cyclopropenyl radical were optimized with the constraints of C_{2v} symmetry and planarity, and are depicted in Fig.2. The two geometries are in agreement with the previous result using a CI electronic wavefunction.[19] These structures are not stable with respect to the out-of-plane vibrational modes. The normal vibrational frequencies and their symmetry assignments in the ethylenic and allylic structures are summarized in Table 1. We shall use the two in plane normal vibrational modes to define the pseudo rotation coordinate in the vicinity of each structure of the cyclopropenyl radical.

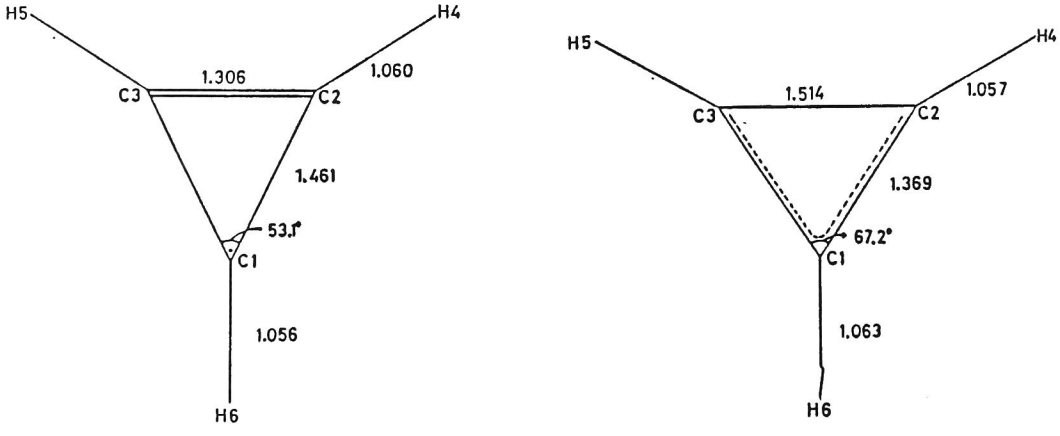

Fig. 2 The optimized geometries of the planar ethylenic and allylic structures of cyclopropenyl radical. The C_{2v} symmetry is assumed.

Table 1 Harmonic vibrational frequencies(cm^{-1}) for the C_{2v} in-plane ethylenic and allylic structure of cyclopropenyl radical

ethylenic		allylic	
b_2	970.0	b_2	847.0
a_1	1033.7	a_1	902.7
b_2	1111.3	b_2	1062.7
a_1	1303.4	a_1	1129.9
b_2	1495.0	b_2	1255.9
a_1	1770.0	a_1	1562.0
b_2	3502.9	a_1	3453.7
a_1	3521.9	b_2	3524.4
a_1	3568.0	a_1	3559.4
out of plane mode		out of plane mode	
b_1	1039.1i	a_2	672.9i
b_1	707.9	b_1	577.3i
a_2	991.7	b_1	922.9

These modes correspond to the minimum frequencies in the plane, which play a central role in the electron rearrangement process as shown in Sec. IIB. The two in-plane normal vibrational modes for each of the ethylenic and allylic structures are depicted in Figs.3(a) and 3(b), respectively.

The pseudo rotation coordinate is defined by;

$$\delta\vec{x}_\alpha=\vec{\upsilon}_{a_1,\alpha}\rho\cos\theta+\vec{\upsilon}_{b_2,\alpha}\rho\sin\theta, \tag{26}$$

where $\delta\vec{x}_\alpha$ and ρ are, respectively, a displacement vector of α-th nucleus of the molecule from the center of a circle and a radius of the circle, $\vec{\upsilon}_{a_1,\alpha}$ and $\vec{\upsilon}_{b_2,\alpha}$ are, respectively, the normal vibrational mode vectors of the α-th nucleus with a_1 and b_2 components of the C_{2v} symmetry. The radius and the center of the circle are determined so as to make the molecule have an equilateral triangle structure with respect to their Carbon skeleton, when the molecule distorts along the normal vibrational mode of the a_1 symmetry. Then the pseudo rotational coordinate is θ. The center and the radius are different for each structure, ethylenic and allylic. Then we shall focus our interest on the electronic response property to the molecular vibration along the pseudo rotation coordinate in the vicinity of the two structures. A schematic representation of the pseudo rotation coordinate (depicted by the solid line), the cell structure[13(b),14(b)] of the potential energy surface (depicted by the broken line) and the equipotential line (depicted by the dotted line) are shown in

(a)

Ethylenic Vibrational Mode

(b)

Allylic Vibrational Mode

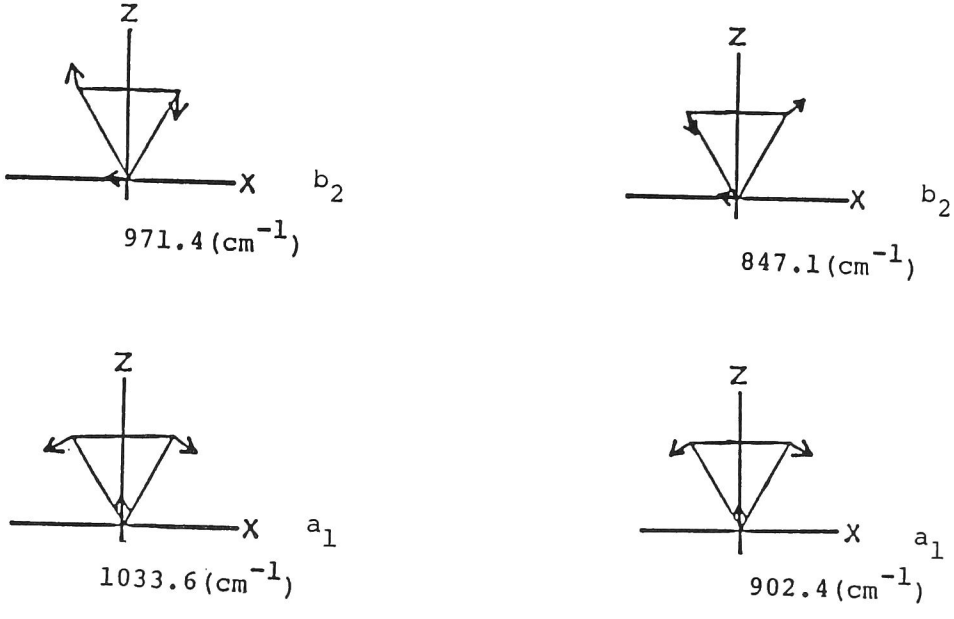

Fig. 3 The in-plane vibrational modes of the ethylenic and allylic structures of cyclopropenyl radical.

Fig.4. The cell structure,[13(b),14(b)] which is constructed from the neighboring domain to the stationary point of the potential energy surface is important because it imposes the boundary condition of the nuclear wavefunction. An elucidation of the cell structure from the electronic structural point of view is interesting in the light of the flexibility of the electronic structure.

B. THE CELL STRUCTURE OF THE POTENTIAL ENERGY SURFACE AND ELECTRONIC FLEXIBILITY

We will investigate the response of the electronic structure to the molecular vibration to clarify the flexibility of the electronic structure of cyclopropenyl radical unit. Before proceeding to investigate this problem, we will compare the transformation property of the rearrangement operators R_{ij} and $R_{ij}^{(2)}$. The operators R_{ij} and $R_{ij}^{(2)}$ are equivalent if and only if the Taylor series expansion of R_{ij} converges up to the second order of Δs (Eq.(8a)) and hence the electron orbital converges within the same order of the expansion. Numerical calculation shows that this is not always true. The MO coefficients of the isomorphic electron orbitals $\tilde{\psi}_k$, which are obtained from the operator R_{ij} and $R_{ij}^{(2)}$ of the allylic cyclopropenyl radical on the pseudo rotation coordinate with θ=25° are tabulated in Tables

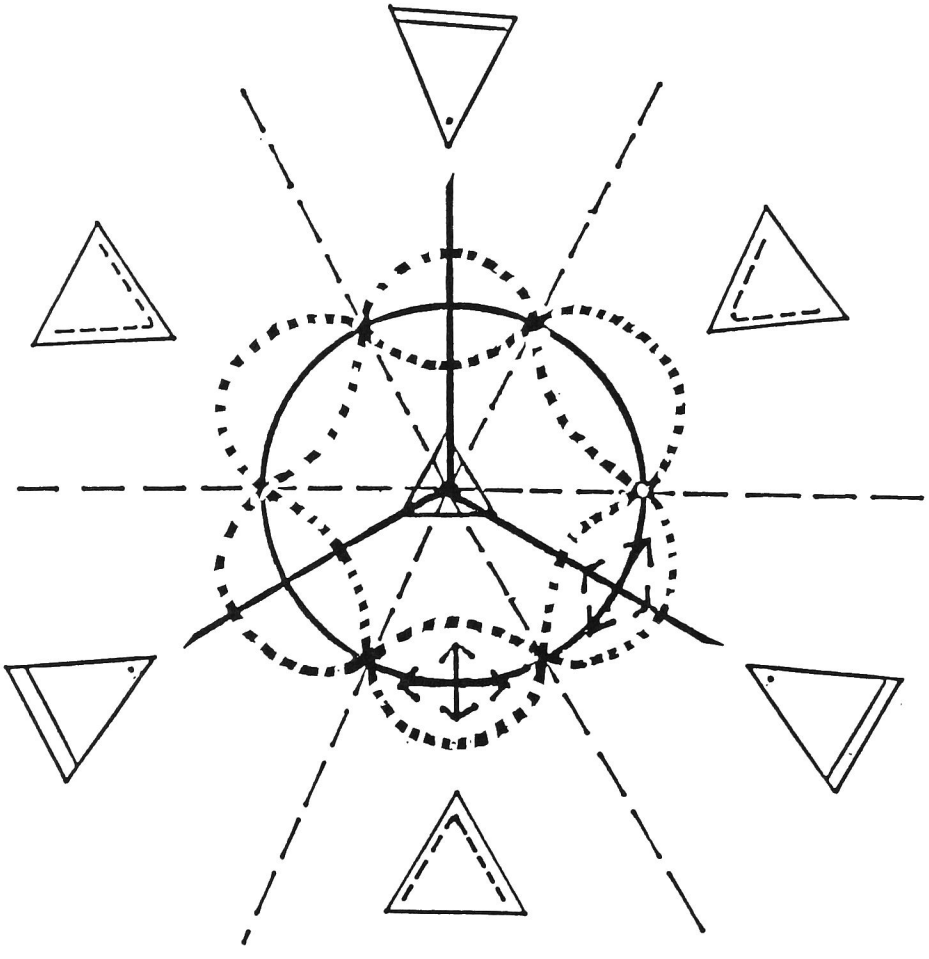

Fig. 4 The schematic representation of the pseudo rotation coordinate, the cell structure of the potential surface, and the equipotential line. The two pseudo rotation coordinates passing through the ethylenic and allylic structures, respectively, are adopted.

2 and 3 with their orbital energies and occupation numbers. From here in this paper, the space of rearrangement operator, i.e. the running range of the suffix of the matrices in Eq.(2) and Eq.(8) is limited to the three π orbitals, one of which is doubly occupied, another is singly occupied, and the other is virtual within the UHF scheme. The orbital patterns of $\tilde{\psi}_2$s obtained from R_{ij} and $R_{ij}^{(2)}$ are not quite equivalent and the orbital energies and the occupation numbers are also different for those obtained from R_{ij} and $R_{ij}^{(2)}$. The properties of the orbitals obtained from $R_{ij}^{(2)}$ are rather similar to the canonical orbitals. Near the origin of the pseudo rotation coordinate, R_{ij} and $R_{ij}^{(2)}$ are quite equivalent. This means that electron orbitals $\{\psi_k\}$ do not converge so soon at the critical point region of the potential energy surface in the Taylor series expansion by Δs . On the other hand, electron orbitals $\{\tilde{\psi}_k\}$ converge very soon near the origin of the pseudo rotation coordinate in the same expansion. The fact that the occupation number changes of the electron orbitals obtained from R_{ij} along of the pseudo rotation coordinate are larger than those of $R_{ij}^{(2)}$ suggests that the continuity of the electron orbitals and hence the quantum effect of molecular vibration affect more the rearrangements of the electrons than does the kinetic energy of molecular vibration. We shall use R_{ij} , because we are interested in the electron orbitals which represent the smooth electron current accompanying a molecular

Table 2 The occupation numbers, the orbital energies, and the expansion coefficients of the transformed orbitals obtained from R_{ij} at $\theta=25^{\circ}$

				$\tilde{\nu}$	0.80035	0.61988	0.57977
				$\tilde{\varepsilon}$	-0.18469	-0.25108	-0.15688
1	C	1S			0.00000	-0.00000	0.00000
		2S	(I)		-0.00000	0.00000	-0.00000
		2PX	(I)		0.00000	-0.00000	0.00000
		2PY	(I)		-0.05155	0.42238	0.18038
		2PZ	(I)		-0.00000	0.00000	-0.00000
		2S	(O)		0.00000	-0.00000	0.00000
		2PX	(O)		0.00000	-0.00000	0.00000
		2PY	(O)		-0.27387	0.64061	0.53178
		2PZ	(O)		0.00000	-0.00000	0.00000
2	C	1S			-0.00000	0.00000	-0.00000
		2S	(I)		-0.00000	-0.00000	0.00000
		2PX	(I)		0.00000	0.00000	0.00000
		2PY	(I)		-0.24431	0.17520	-0.51456
		2PZ	(I)		-0.00000	0.00000	-0.00000
		2S	(O)		0.00000	-0.00000	0.00000
		2PX	(O)		-0.00000	0.00000	-0.00000
		2PY	(O)		-0.29827	0.00893	-0.58598
		2PZ	(O)		0.00000	0.00000	0.00000
3	C	1S			-0.00000	0.00000	0.00000
		2S	(I)		0.00000	-0.00000	0.00000
		2PX	(I)		0.00000	0.00000	0.00000
		2PY	(I)		0.53008	0.15948	-0.14010
		2PZ	(I)		-0.00000	-0.00000	-0.00000
		2S	(O)		-0.00000	-0.00000	-0.00000
		2PX	(O)		-0.00000	0.00000	-0.00000
		2PY	(O)		0.70048	-0.07603	-0.21738
		2PZ	(O)		0.00000	-0.00000	0.00000
4	H	1S	(I)		0.00000	0.00000	-0.00000
		1S	(O)		-0.00000	0.00000	-0.00000
5	H	1S	(I)		0.00000	-0.00000	0.00000
		1S	(O)		-0.00000	0.00000	-0.00000
6	H	1S	(I)		-0.00000	0.00000	-0.00000
		1S	(O)		0.00000	-0.00000	0.00000

Table 3 The occupation numbers, the orbital energies, and the expansion coefficients of the transformed orbitals obtained from $R_{ij}^{(2)}$ at $\theta=25°$

				$\tilde{\nu}$	1.00000	0.99780	0.00220
				$\tilde{\varepsilon}$	-0.52088	-0.25430	0.18254
1	C	1S			0.00000	0.00000	-0.00000
		2S	(I)		-0.00000	-0.00000	0.00000
		2PX	(I)		0.00000	0.00000	-0.00000
		2PY	(I)		-0.21669	0.06114	0.40362
		2PZ	(I)		-0.00000	-0.00000	0.00000
		2S	(O)		0.00000	0.00000	-0.00000
		2PX	(O)		0.00000	0.00000	-0.00000
		2PY	(O)		-0.13135	0.04810	0.86522
		2PZ	(O)		0.00000	0.00000	-0.00000
2	C	1S			-0.00000	-0.00000	0.00000
		2S	(I)		0.00000	0.00000	0.00000
		2PX	(I)		-0.00000	0.00000	-0.00000
		2PY	(I)		-0.35728	-0.45656	-0.13806
		2PZ	(I)		-0.00000	-0.00000	0.00000
		2S	(O)		0.00000	0.00000	-0.00000
		2PX	(O)		-0.00000	-0.00000	0.00000
		2PY	(O)		-0.25192	-0.54556	-0.26704
		2PZ	(O)		0.00000	0.00000	-0.00000
3	C	1S			-0.00000	-0.00000	0.00000
		2S	(I)		0.00000	0.00000	-0.00000
		2PX	(I)		-0.00000	0.00000	0.00000
		2PY	(I)		-0.34794	0.40062	-0.21091
		2PZ	(I)		0.00000	-0.00000	-0.00000
		2S	(O)		-0.00000	-0.00000	-0.00000
		2PX	(O)		-0.00000	-0.00000	0.00000
		2PY	(O)		-0.25285	0.50140	-0.47788
		2PZ	(O)		0.00000	0.00000	-0.00000
4	H	1S	(I)		-0.00000	-0.00000	0.00000
		1S	(O)		-0.00000	-0.00000	0.00000
5	H	1S	(I)		0.00000	0.00000	-0.00000
		1S	(O)		0.00000	-0.00000	0.00000
6	H	1S	(I)		-0.00000	-0.00000	0.00000
		1S	(O)		0.00000	0.00000	-0.00000

vibration.

The canonical SOMO and LUMO orbitals; ψ_{SOMO} and ψ_{LUMO}, are drawn schematically in Fig.5. The isomerization between the allylic and ethylenic structures must go through a SOMO-LUMO crossing. The correlation diagrams between the orbital energy $\{\tilde{\varepsilon}_k\}$ and the occupation number $\{\tilde{\nu}_k\}$ defined by Eq.(7) and (6.a), respectively are calculated. The rearrangement of the orbital occupation numbers are very small in the ethylenic cell, as is shown in Fig.(6.a). On the contrary, the occupation number of $\tilde{\psi}_1$, which has a LUMO orbital pattern, of the allylic cyclopropenyl radical from $\theta = 5°$ to $\theta = 25°$ increases throughout accompanying the isomerization reaction in the allylic cell. The orbital energy of $\tilde{\psi}_1$ decreases meanwhile. The occupation numbers of $\tilde{\psi}_3$ and $\tilde{\psi}_2$ whose orbital patterns are the totally symmetric and the SOMO of the allylic cyclopropenyl radical decreases during the isomerization. The orbital energies of $\tilde{\psi}_3$ and $\tilde{\psi}_2$ increase meanwhile. The electrons are transported from the orbitals $\tilde{\psi}_3$ and $\tilde{\psi}_2$ to the orbital $\tilde{\psi}_1$, and this characterizes the initial electronic process of the isomerization reaction from the allylic structure to the ethylenic structure. Then it can be said that the response of the electronic structure to the molecular vibration is small and hence the electronic structure is solid in the ethylenic cell. In contrast the response is large and the electronic structure is soft in the allylic cell. Moreover

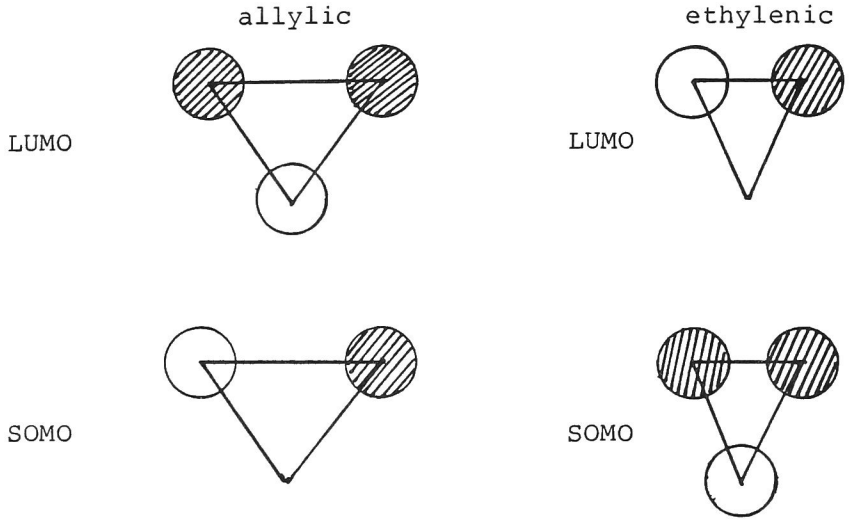

Fig. 5 The orbital patterns of the LUMO and SOMO orbitals of the ethylenic and allylic structures of cyclopropenyl radical

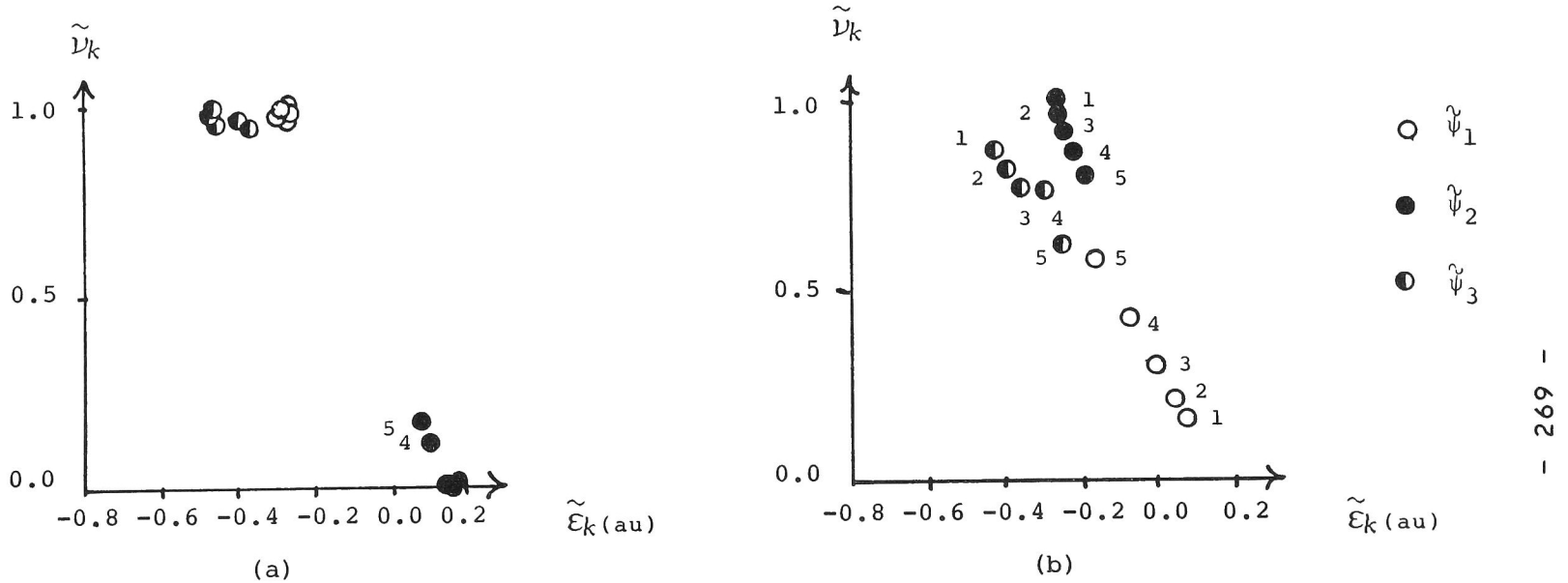

Fig. 6 The changes of the α-electron orbital energy-occupation number correlation diagram of the ethylenic(a) and allylic(b) structures of cyclopropenyl radical.
$\tilde{\psi}_1$ denotes LUMO(SOMO) pattern of the allylic(ethylenic) structure,
$\tilde{\psi}_2$ denotes SOMO(LUMO) pattern of the allylic(ethylenic) structure, and
$\tilde{\psi}_3$ denotes the electron orbital which has a totally symmetric pattern。
The changes are traced along the pseudo rotation coordinate, and the number 1, 2, 3, 4, and 5 denote that θ is 5°, 10°, 15°, 20°, and 25°.

the ethylenic cell can be said to be larger than the allylic one judging from the response property of the electronic structure.

IV. CONCLUDING REMARKS

As the electronic structure is flexible in the isomerization channel of the allylic cyclopropenyl radical, it may not be suitable for the valve unit of the tetracyclic soliton valve, because the isomerization channel will perturb the action of the valve in that case. The ethylenic cyclopropenyl radical may be suitable, because the electronic structure is solid and then the isomerization channel is closed. Our calculation indicates that one should try to fabricate the soliton valve so as to make the valve unit to have ethylenic structure in the 3D and 6B states.

We have applied the isomorphic electron orbitals to the problem of the molecular design of the soliton valve. The transformation properties of the rearrangement operator are discussed analytically and numerically by presenting the derivative expression of the operator. The isomorphic electron orbitals are shown to present a good starting point on the study of the vibronic problem.

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Chapter 5

Conclusion

In part III of this thesis, the smooth electron rearrangement described by the electron orbitals which change as little as possible accompanying their evolution along the IRC is studied.

In chapter 2 of this part, the two sets of electron orbitals on two neighboring points separated by an infinitesimal distance on the reaction coordinate are transformed so as to make them have a one-to-one correspondence using the criterion of their overlap integrals. The occupation numbers of the transformed orbitals are defined naturally on the basis of the diagonal element of the first order density matrix. The electron orbitals and their occupation numbers are traced along the IRC of the radical reaction; $CH_3 + HF \rightarrow CH_4 + F$. The space distributions of the transformed orbitals are calculated to be almost invariant along the IRC. Moreover, the two characteristic transformed orbitals which strongly localize on the 2p orbitals of the C atom and the F atom, respectively are obtained, though the transformation operator itself does not contain any localization terms, such as self-energy integrals. On the other hand, the occupation numbers of the two localized orbitals change drastically, though the other occupation

numbers do not change so much. This characterizes the electronic process of the reaction, and agrees with the results of the analysis of the dynamic electron transfer accompanying the motion of the wavepacket along the IRC and the analysis of the canonical orbitals. In addition, it enables us to present a new picture of the electronic process of the chemical reaction, which is represented through the rearrangement of the occupation numbers between the transformed orbitals.

In chapter 3 of this part, the orbital energies of the transformed orbital are traced to give a characteristic change of the orbital energy-occupation number correlation diagram along the IRC of the radical reaction; $CH_3 + HF \rightarrow CH_4 + F$ The orbital energies of the transformed orbitals are defined naturally by using the diagonal elements of the Fock matrix of the canonical orbitals. The energy of the orbital whose occupation number increases stabilizes greatly, and the energy of the orbital whose occupation number decreases becomes unstable. The mode specific feature of the dynamic electron transfer of the reaction is studied also. The dynamic electron transfer along the IRC is studied for the radical reaction; $CH_3 + CH_4 \rightarrow CH_4 + CH_3$. All these results are used to elucidate the interchain electron transport between the two polyacetylene chains and the dopant-chain electron transfer of polyacetylene through the locally isomorphic chemical reaction

analogue model.

In chapter 4 of this part, the derivative expression for the transformation operator is deduced. The difference of the transformation operator expressed by the derivatives of electron orbitals and the original transformation operator is studied numerically. They do not always coincide with each other, because of the slow convergence of the Taylor series expansion of the electron orbitals by the nuclear coordinates. The transformation operator expressed by the derivatives of the electron orbitals has a relation with the nonadiabatic energy of a molecule. The trace of the operator coincides with the nonadiabatic energy of the molecule in a certain condition. It also has a relation to the nonadiabatic coupling term of the dynamic Fock equation. The quantum mechanical treatment of the nuclear vibration in the formulation of the rearrangement operator is introduced to study the effect of the local quantum fluctuation in the nuclear motion on the rearrangement of electrons. The stable limit theorem predicts that the rearrangement of electrons is largest when the nuclei move along the IRC. The response of the electronic structure to the molecular vibration is studied by tracing the change of the occupation numbers of the electron orbitals along the schematic reaction coordinate of the isomerization reaction of cyclopropenyl radical. Where the change of the occupation numbers are large, the electrons are said to be flexible to

molecular vibration, and vice versa. The electrons in the allylic isomer of the cyclopropenyl radical are calculated to be flexible, on the other hand the electrons in the ethylenic isomer are calculated to be rigid. This result shows that the allylic isomer easily isomerizes to the ethylenic isomer, but the ethylenic isomer is difficult to isomerize. It might then be beneficial to use an ethylenic cyclopropenyl radical as the unit of the soliton valve whose operation will become complicated if the isomerization channel is open.

Appendix to part III

Rearrangement of the Occupation Number of the Electron Orbital Induced by the Nonadiabatic Motion of Nuclei

The smooth electron current represented by the transformed orbitals and their occupation number in the course of the chemical reactions has been studied in this part.[1-3] The analytical structure of the rearrangement operator whose criterion is obtained in connection with the molecular vibration was also discussed.[3] The analytical expression for the occupation number of the transformed orbital and the transformations of the orbital themselves are unknown and they are clarified through actual numerical calculation. It will be interesting then to investigate the analytical structure of the occupation number of the electron orbital which is influenced by the molecular vibration. Here, the time dependent perturbation method[4] will be used in the discussion of an analytical expression for the occupation number of the electron orbital which deviates from the adiabatic approximation in the time dependent SCF equations.[5,6]

Let $\hat{F}(t)$ be the time-dependent natural orbital Hamiltonian[6-8] of the molecular system, then the time-dependent SCF equations for the natural orbitals $\{\varphi_j(t)\}$

are given as follows;

$$i\hbar(\partial/\partial t)=\hat{F}(t)\varphi_j(t), \tag{1}$$

where t denotes the time parameter. The time dependency of the Hamiltonian is brought in by the time dependent classical nuclear motions as the impact parameter.[9] Suppose the Hamiltonian changes continuously from an initial value $\hat{F}_0$ at the time t_0 to a final value $\hat{F}_1$ at the time t_1;

$$\hat{F}(0)=\hat{F}_0, \qquad \hat{F}(1)=\hat{F}_1, \tag{2}$$

and let $\hat{F}(s)$ be the value of the Hamiltonian at the time $t=t_0+sT$, where the parameter T is given by;

$$T=t_1-t_0 \tag{3}$$

$\hat{F}(s)$ is a continuous function of s and the evolution of the molecular system from time t_0 to time t_1 depends only on the parameter T which is the measure of the speed of the passage from F_0 to F_1. The adiabatic theorem says that if the system is in an eigenstate of $\hat{F}_0$ at the initial time, it will also be an eigenstate of $\hat{F}_1$ at the time t_1 in a certain condition. Only the phase factor changes. The eigenstate is given as the solution of the following equation;

$$\hat{F}(t)\psi_j(t)=\varepsilon_j(t)\psi_j(t), \tag{4}$$

where $\varepsilon_j(t)$ is the orbital energy of the electron orbital which depends only parametrically on t. The deviation from the adiabatic approximation is given by the time dependent perturbation method.[4] The electron orbital $\{\tilde{\psi}_j(t)\}$ which deviates from the adiabatic approximation up to the second

order is given under the assumption that the average field of the electrons does not change, as follows;[4]

$$\tilde{\psi}_k \sim \exp\left[-i/\hbar \int_0^t \varepsilon_\kappa(\tau)d\tau\right]$$

$$\times\left[\psi_k + i\hbar\sum_j \{\langle\psi_j|\dot{\psi}_k\rangle/(\varepsilon_j-\varepsilon_k)\}\psi_j\right.$$

$$\left.+\hbar^2\sum_j\sum_i \{\langle\dot{\psi}_j|\psi_i\rangle\langle\psi_i|\dot{\psi}_k\rangle/(\varepsilon_j-\varepsilon_i)(\varepsilon_j-\varepsilon_k)\}\psi_j\right], \qquad (5)$$

where $\dot{\psi}_j$ denotes the time derivative of ψ_j. The occupation number $\tilde{\nu}_k(t)$ of the electron orbital $\tilde{\psi}_k(t)$ is defined naturally as follows;[1-3]

$$\tilde{\psi}_k \equiv (1/N_k)\langle\tilde{\psi}_k|\rho|\tilde{\psi}_k\rangle, \qquad (6)$$

where $N_k(t)$ is the norm of the electron orbitals $\tilde{\psi}_k(t)$ and $\rho(t)$ is the diagonal element of the first order density matrix represented by the natural orbitals $\{\psi_j(t)\}$;[10]

$$\rho = \sum_j |\psi_j\rangle\nu_j\langle\psi_j|. \qquad (7)$$

The time dependencies are implicit in Eqs.(5),(6),(7), and from now on. From Eqs.(5),(6), and (7), the occupation number is given up to the second order as follows;

$$\tilde{\nu}_k \sim \left[\nu_k + \hbar^2\sum_n \nu_n\{\langle\dot{\psi}_k|\psi_n\rangle\langle\psi_n|\dot{\psi}_k\rangle\}/(\varepsilon_n-\varepsilon_k)^2\right]/\left[1\right.$$

$$\left.+\hbar^2\sum_n \{\langle\dot{\psi}_k|\psi_n\rangle\langle\psi_n|\dot{\psi}_k\rangle\}/(\varepsilon_n-\varepsilon_k)^2\right] \qquad (8)$$

The orbital energy $\tilde{\varepsilon}_k$ of the electron orbital $\tilde{\psi}_k$ may be similarly defined and it is approximately obtained as follows;

$$\tilde{\varepsilon}_k \sim \left[\varepsilon_k + \hbar^2 \sum_n \varepsilon_n \{ \langle \dot{\psi}_k | \psi_n \rangle \langle \psi_n | \dot{\psi}_k \rangle \} / (\varepsilon_n - \varepsilon_k)^2 \right] / \left[1 + \hbar^2 \sum_n \{ \langle \dot{\psi}_k | \psi_n \rangle \langle \psi_n | \dot{\psi}_k \rangle \} / (\varepsilon_n - \varepsilon_k)^2 \right] \quad (9)$$

The equations (8) and (9) show how the nuclear motions act to rearrange the electrons of the molecular system in the electron orbital manifold. The expression of the occupation number $\tilde{\nu}_k$ given by Eq.(8) is important for the couplings between the nuclear motions and the electron correlation.

In the Hartree-Fock approximation,[11] the occupation number of the LUMO orbital is given approximately by;

$$\tilde{\nu}_{LUMO} \sim \left[2\hbar^2 | \langle \dot{\psi}_{HOMO} | \psi_{LUMO} \rangle |^2 / (\varepsilon_{HOMO} - \varepsilon_{LUMO})^2 \right] / \left[1 + \hbar^2 | \langle \dot{\psi}_{HOMO} | \psi_{LUMO} \rangle |^2 / (\varepsilon_{HOMO} - \varepsilon_{LUMO})^2 \right]. \quad (10)$$

which shows that the most important contribution to the dynamically induced promotion of the electron to the LUMO orbital comes from the HOMO orbital of the molecular system and it is largest if the nuclei moves to maximize $| \langle \dot{\psi}_{HOMO} | \psi_{LUMO} \rangle |^2$. The functional form of the right hand side of Eq.(10) is shown in Fig.1. The analysis discussed here elucidates how the vibronic interaction induces the rearrangement of the electrons in the molecular system on the basis of the natural orbital Hamiltonian which can well describe the electron correlation. The assumption that the average field does not change as the electron orbitals deviate

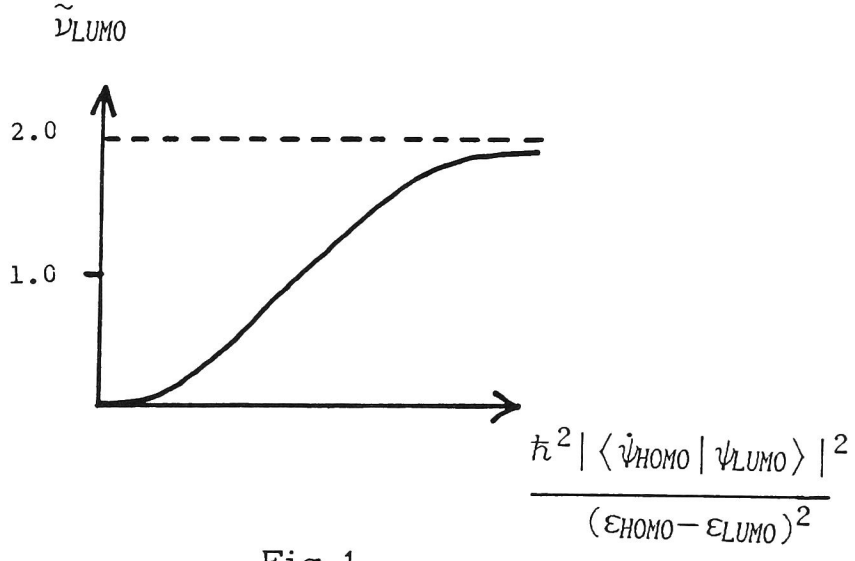

Fig.1

The functional form of Eq.(10).

from the adiabatic approximation is considered to be valid where the total energy exchange between the nuclear motions and the electronic motions are small. The detailed study of the occupation number which does not require this assumption will be possible if the time dependent perturbation method is applied directly to the total molecular time dependent Schrödinger equation and if the natural orbital is constructed from the total wavefunction. This will not be difficult but is tedious. The analysis discussed in this appendix does not restrict the perturbation only to the nuclear motions. Other perturbations such as external field effects can be treated with the same equation.

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General Conclusion

The mechanism of the vibronic interaction in the chemical reacting system has been studied.

In part I, the exact equation which describes the coupling between the electronic motion and the nuclear motion is developed on the basis of the variational principle familiar in traditional quantum chemistry. The equation determines the electron orbital which reflects the dynamics of the molecular vibration; the nonadiabatic effect and the quantum effect. The effects from the different parts of the molecular interactions; the dynamics of the molecular vibration and the electronic average field of the molecule are incorporated into the one electron orbital equation. Then, it can be said that this equation makes it possible to renormalize the electronic motion affected by the molecular vibration. The dynamic electron density which reflects the quantum effect of the molecular vibration is studied in this context. The novel additive property of the dynamic electron density which predicts that the change of the electron density due to the excitation of the molecular vibration is proportional to the difference in quantum number of the molecular vibration is proved and calculated to be large enough to be observed experimentally. The time-dependence of the coherently driven dynamic electron density is shown to

have the new quantum-classical correspondence relation. The dynamic electron densities and their time dependence are analyzed for various molecules to obtain the new dynamic aspects of the chemical bonding and the chemical stabilities of the reactive species. In the appendix to part I, the effects of the intense radiation field as well as the molecular vibration upon the electronic structure of the molecule are incorporated into the one electron orbital equation. This equation will be important in the study of the nonlinear optical property of the molecular system where the vibronic interaction cannot be neglected.

In part II, the dynamic electron current induced by the quantum effect of the wavepacket of the nuclear motion in the course of the chemical reaction process is studied. Some dynamical aspects inherent in the chemical reaction such as the isotopic effect, the vibrational mode specificity, and the energy transfer process between distinct vibrational modes are studied to discuss how these affect or concern the electron current in the course of the chemical reaction process. The vibrationally induced dipole fluctuation between the chemical reacting species is analyzed also. The vibrationally induced long-range interaction will be important. This is ascertained in the appendix to part II, where the exsistence of the novel intermolecular force originated in vibronic coupling is demonstrated.

In part III, the electron orbital which changes as little as possible in the course of the chemical reaction process is defined by introducing a one-to-one correspondence between the two sets of the electron orbitals on the two neighboring points separated by the infinitesimal distance on the reaction coordinate. The one-to-one correspondence in the criterion of the overlap integrals between the two electron orbitals on the two distinct points are obtained in terms of the Amos-Hall correspondence orbital transformation. The transformed electron orbital represents the smooth electron rearrangement in the course of the chemical reaction process. The numerical calculation shows that the transformed orbital localizes strongly though there is no localization criterion in its definition. The occupation number of the transformed orbital can be naturally defined in terms of the occupation number of the original natural orbital. The energy of the transformed orbital can also be defined in terms of the energy of the original canonical orbital when the Hartree-Fock approximation is used. Numerical calculations are carried out to show the characteristic change of the occupation number-orbital energy correlation diagram in terms of the transformed orbital for chemical reacting systems. The mathematical relations between the rearrangement operator of the transformed orbital and the nonadiabatic correction terms are discussed along with the numerical calculations to test

the validity of the approximation used in that discussion. The analytical expression for the occupation number of the electron orbital which deviates from the adiabatic approximation accompanying the parametrical change of the nuclear coordinates is discussed in the appendix of part III in terms of the time-dependent perturbation method with certain assumptions. An interesting behaviour of the occupation number near to the Fermi level is obtained. The discussions given in part III insist that a careful consideration is necessary when the electronic process in the chemical reaction is discussed by means of the electron orbital accompanying the parametric change of nuclear coordinates, if one wants to analyze the smooth electronic rearrangement inherent in the chemical reacting system.

The mechanism of the vibronic interaction in the chemical reacting system has been studied from the two points of view discussed in the preface of this thesis; the renormalization concept and the adiabatic continuity. The renormalization of the molecular eigenstate under the radiation field of all ranges of wavelength, which also takes into account the vibronic interaction is a difficult problem. The nonadiabatic effects are necessarily concerned with the internal electromagnetic or radiation field in the material. The nonlinear optical properties of the vibronic systems will hence be an interesting problem to be studied theoretically.

The guage theory will be important. The change of the wavefunction accompanying the parametrical change of the nuclear coordinates brings in the path dependent phase factor change. The phase factor change may be observed according to the discussion given by Aharanov. In terms of the guage theory, the phase factor is clearly related to the electromagnetic field. Again the vibronic interaction in the background electromagnetic field will be an important problem for theoretical chemistry. Sometimes, a large scale numerical computation will be important. The numerically reinforced theoretical chemistry and the theoretically reinforced computational chemistry will give the best hope of development toward these ends. I will close this thesis with this conclusion.